THE REACTION BETWEEN HYDROGEN AND OXYGEN

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PREFACE

The reaction between hydrogen and oxygen is of fundamental importance chemically, and kinetically has proved to have remarkable characteristics. Many papers on the subject have appeared during the past few years, and some general account now seems called for. In this monograph a unified treatment has been adopted as far as possible. We have considered the subject in the light of all the available evidence, and adopted what has seemed to be the best conclusion. Thus the views now expressed do not always correspond to those to be found in any individual original paper.

We have tried to explain the theoretical principles as simply as possible, so that the book might be of assistance to students, and of interest to those who are not specialists in chemical kinetics.

C. N. H.
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unused to the complexity of nature would probably expect the reaction

$$2H_2+O_2 = 2H_2O$$

to be determined by the simultaneous encounter of two molecules of hydrogen and one molecule of oxygen, and the rate of formation of water to be proportional to the product $[H_2]^2[O_2]$. In this he would, of course, be mistaken, for the interaction of these two simple gases gives rise to a series of phenomena as varied as they are remarkable.

In the first place the reaction is very sensitive to catalytic influences. Some metals in a finely divided state are able to cause combination even at the ordinary temperature, while above 500° C., where the gas reaction comes into prominence, the walls of the reaction vessel still have to be taken into account. The action of different surface catalysts depends upon the adsorption of the gases, and many different types of behaviour are met with. These are exemplified in Chapter II.

The reaction occurring in the gas phase can be investigated between 500° and 600° C. if it is induced thermally, and at the ordinary temperature when brought about by photochemical means. It owes its peculiar characteristics to the fact that it is a chain reaction. It is indeed one of the best examples of this type of chemical transformation.

The thermal reaction can be caused to take place at a controllable and measurable speed in a certain range of temperature and pressure. Increase of either may increase the speed so greatly that the heat liberated in the system cannot be conducted away, and the gases inflame. This, however, is not the only way in which ignition occurs. If, in the region of measurable velocity, the pressure is lowered, a point may be reached at which the gases suddenly inflame, even though at a slightly higher pressure their rate of reaction was very slow. An upper and a lower limit of pressure bound the region where this unexpected ignition can occur. The effect can be explained in terms of a theory of 'branching chains', and is discussed in Chapter VI.

Once explosion has set in, many new phenomena make their appearance, and it is not always quite easy to decide whether they are inherently part of the reaction mechanism, or secondary effects of the high temperature produced by the flame. For example, ionization occurs to some extent. This raises the question whether ionization is necessary for gaseous reactions. As a matter of fact it appears to be secondary in this particular case, Garner and Saunders† having found that the small ionization produced is about what might be expected from the maximum temperature of the explosion without any chemical effects.

In the same way, the spectrum of hydroxyl appears in a hydrogen-oxygen flame, but we can hardly say whether it is not produced by the thermal dissociation of steam, since it appears also in the absorption spectrum of steam at high temperatures.

The burning of hydrogen in oxygen, as with other combustible gas mixtures, may become so violent as to give rise to a detonation wave. The question of the actual propagation of explosion waves is a very complex problem involving not only chemical but hydrodynamical considerations. For this reason, and because of the difficulty of obtaining an insight into the actual kinetic mechanisms by such means, it has been omitted from the present treatment. For the properties of the flame, reference should be made to special works on the subject.‡ The same complexity makes it difficult to draw purely chemical deductions from experiments on the passage of electrical discharges through gases. Since it would be beyond our scope to go into the difficult question of the nature of the electrical processes occurring in various regions of a discharge, this important subject will only be referred to here.†

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† Garner and Saunders, *Trans. Faraday Soc.*, 1926, **22**, 342.

‡ e.g. Bone and Townend, *Flame and Combustion in Gases*, where the classical work of H. B. Dixon and others is described.

Experiments on the intensive drying of hydrogen-oxygen mixtures have seemed to show that explosion may be prevented under conditions where it would normally have occurred. Such a conclusion has its difficulties, for the investigators who reported such results also stated that the explosion was sometimes replaced by a slow reaction. It is evident that the earlier stages of such a process produce water vapour which should have the same effect as the incompletely removed moisture present under ordinary conditions, and explosion should ensue. The fact that it does not makes it difficult to neglect the possibility that inhibiting substances were introduced into the system during the drying process.

In the following pages the various ways in which the combination of oxygen and hydrogen can take place will be considered in turn. The surface reaction will be taken first, the catalytic influence of surfaces representing, in one sense, the easiest way in which the resistance of the gases to chemical change can be overcome. In general, this influence of the surface depends upon a lowering of the energy of activation required by the reacting substances in the adsorbed condition. There is no reason to doubt that the general principle is applicable in the present special example. The photochemical change will be considered next. Here there is little doubt that the reaction depends upon the primary formation of atoms from the hydrogen or from the oxygen. The study of their possible fates in the reaction mixture gives valuable information about various types of chain process. This knowledge, in conjunction with various energetic considerations, outlined in a special chapter, is ultimately of great assistance in interpreting the chemical nature of the chain reactions occurring in the thermal interaction of the two gases at higher temperatures. The thermal reaction itself possesses many remarkable characteristics. These can be explained to a large extent without the introduction of precise assumptions about the chemical nature of the chains. Consequently, what may be called the physics of the various phenomena will be treated first, and the correlation of the physical and the purely chemical evidence attempted in a special chapter at the end. In some ways this will prove the most speculative part of the whole investigation. Hence it is advantageous to separate it to some extent from the rest.

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† See Finch and others, *Proc. Roy. Soc.*, 1931, A, **133**, 173; 1934, A, **143**, 482.

II

THE SURFACE REACTION

THE effect of platinum surfaces on mixtures of hydrogen and oxygen was demonstrated by Erman and later by Döbereiner,† who found that explosions would occur even at room temperature when suitably prepared platinum was introduced into the gas. Dulong and Thénard‡ extended this investigation to include surfaces of gold, silver, and glass, but the explosion was the object of interest and the surface reaction itself received no separate treatment.

Henry§ showed that spongy platinum behaved selectively towards mixtures of various combustible gases with oxygen, for hydrogen and carbon monoxide could be easily oxidized at temperatures where hydrocarbons were almost unaffected. This investigation was the origin of the methods of preferential combustion which have been applied so successfully to gas analysis.

Faraday's|| investigations of the hydrogen-oxygen voltameter showed that the gases evolved by the apparatus were partially lost after standing for some time. The careful elimination of all other possibilities led him to the conclusion that the platinum electrodes were causing recombination of the mixed gases with consequent water formation, and that the efficiency of the platinum decreased with use. The deductions that he drew from these results are in remarkable agreement with our modern ideas of catalytic processes.

The work of Faraday and his contemporaries differs from modern investigations of the reaction in that more

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† Döbereiner, *Schweigger's Journ.*, 1822, **34**, 91; 1823, **38**, 321.

‡ Dulong and Thénard, *Ann. Chim. Phys.*, (ii) 1823, **23**, 440; 1823, **24**, 380.

§ Henry, *Phil. Mag.*, 1825, **65**, 269.

|| Faraday, *Phil. Trans.*, 1834, **55**, 114.

emphasis is now placed upon a detailed study of factors influencing the velocity of water formation. In order to appreciate the results obtained by recent investigators it is necessary to give a brief outline of certain parts of the present-day theory of surface catalysis.†

First of all, reaction occurs only after adsorption of one or all of the reactants. In the combination of hydrogen and oxygen the results indicate that, in general, both gases are adsorbed, but the possibility of one being adsorbed and reacting when the other strikes it from the gas phase is not excluded.

The surface available for adsorption depends on many complex factors, but the fraction of such surface that is actually occupied is fairly well represented by the Langmuir isotherm,

$$\sigma = \frac{bp}{1+bp},$$

where σ is the fraction occupied, p is the gas phase pressure when equilibrium is established, and b is a constant.

There are two important limiting conditions for this expression. At very low pressures ($bp \ll 1$)

$$\sigma \simeq bp,$$

that is, the fraction covered by gas is a linear function of the pressure. When the pressure is sufficiently great ($bp \gg 1$) we find

$$\sigma \simeq 1,$$

indicating complete covering of the available surface. When the velocity of reaction is directly proportional to the surface covered we shall find a linear relation between velocity and gas pressure if the latter is sufficiently small. However, when the pressure is brought to a point at which $\sigma \simeq 1$ the velocity will remain unchanged in spite of subsequent pressure increases and we have a zero-order reaction:

$$dx$$

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† Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1918, **40**, 1361.

When two gases are adsorbed without interfering with one another, their surface concentrations can be expressed by separate isothermal formulae, for example,

$$\sigma_A = \frac{}{1+bp_A} \qquad \sigma_B = \frac{}{1+b'p_B}.$$

However, if the two gases compete for the same portions of the surface, the isotherms become

$$\sigma_A = \frac{bp_A}{1+bp_A+b'p_B} \qquad \sigma_B =$$

If B is much more tenaciously adsorbed than A, its adsorption constant b' will be much larger than b. The formulae then reduce to the approximations

$$bp_A \qquad \sigma_B \simeq 1.$$

These relations tell us that the surface is almost completely covered with gas B, and that the small portion covered by A is reduced still more by competition from B. If the surface reaction is bimolecular, that is, if

$$\frac{dx}{dt} = k\sigma_A\,\sigma_B,$$

we obtain

$$\frac{dx}{dt} = k'\frac{p_A}{p_B},$$

indicating that an increase in the pressure of B will cause the reaction velocity to decrease.

In the light of these possibilities we may examine the experimental results.

Bone and Wheeler† investigated the surface reaction by means of a circulatory system in which the steam was condensed and the course of the reaction followed by the pressure variation of the residual hydrogen and oxygen. Many solids were used as contact agents and their ability to 'absorb' hydrogen and oxygen was determined in separate experiments.

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† Bone and Wheeler, *Phil. Trans.*, 1906, A, **206**, 1.

In every case it was found that the reaction velocity was independent of the pressure of oxygen and varied with the first power of the pressure of hydrogen. Furthermore, pretreatment of the surface with hydrogen accelerated the subsequent reaction, but pretreatment with oxygen had no such effect. The 'absorption' experiments led to the conclusion that large quantities of hydrogen could be taken up slowly by the surface and that only a small, rapidly 'absorbed' quantity of oxygen was needed to reach saturation. These results could be generalized for surfaces of gold, silver, platinum, nickel, porcelain, calcined magnesite, and the oxides of iron, manganese, nickel, and copper. The experiments with the oxides were made at temperatures where the rate of the hydrogen-oxygen combination was markedly greater than the rate of reduction of oxide to metal.

The results are what one would expect with a system where the following adsorption relations obtained:

$$\sigma_{O_2} = 1 \qquad \sigma_{H_2} = kp_{H_2},$$

and where the rate-determining process was a collision between adsorbed hydrogen and adsorbed oxygen, leading to the expression

$$\frac{dx}{dt} = k'\sigma_{H_2}\sigma_{O_2} = k''p_{H_2}.$$

The experiments on platinum surfaces have been repeated under somewhat different conditions. Langmuir† used low pressures of hydrogen and oxygen, obtaining the following kinetic expressions:

$$\frac{dx}{dt} = k\frac{p_{O_2}}{p_{H_2}} \quad \text{below } 700^\circ \text{ C.;}$$

$$\frac{dx}{dt} = k'p_{H_2} \quad \text{above } 700^\circ\text{, oxygen in excess;}$$

$$\frac{dx}{dt} = k''p_{O_2} \quad \text{above } 700^\circ\text{, hydrogen in excess.}$$

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† Langmuir, *Trans. Faraday Soc.*, 1922, **17**, 621.

700 at

hydrogen is strongly adsorbed and oxyg

sorbed under the given conditions of temperature and pressure. Above 700° we may assume that the surface is saturated with respect to the gas that is in excess, and that the other is adsorbed independently in such a manner that the adsorption varies with its partial pressure in the gas phase. Another possibility is that reaction takes place when a suitably activated gas molecule of the first strikes an adsorbed molecule

adsorbed gas forms a

At temperatures in the neighbourhood of 150°, which is)° lower than that employed by Bone and Wheeler, the results are again changed if the gas pressures are relatively high compared with those employed in Langmuir's investigations. The reaction velocity is now given by[†]

$$dx$$

whether oxygen or

ms conclude that the

ted with hydrogen and that the dependence of rate on the oxygen pressure is

relation between the amount of oxygen adsorbed

partial pressure. A similar expression[‡] is found for the combination of hydrogen and oxygen on relatively inactive silver surfaces at high temperatures, leading to the same conclusion about the adsorption of the two gases.

The reverse of this result is found in the case of an active silver surface at lower temperatures,[§] the expression being

$$\frac{dx}{dt} = kp_{H_2},$$

[†] Donnelly and Hinshelwood, *J. Chem. Soc.*, 1929, **131**, 1727.

[‡] Hinshelwood, Moelwyn-Hughes, and Rolfe, *Proc. Roy. Soc.*, 1933, A, **139**, 521.

[§] Benton and Elgin, *J. Amer. Chem. Soc.*, 1926, **48**, 3027.

which is in agreement with the result found by Bone and Wheeler at an intermediate temperature. Here again we have evidence indicating that the surface is saturated with oxygen and that the adsorption of hydrogen varies with the first power of its pressure. Later work on the sorption of oxygen by silver† has shown that an actual silver oxide phase is formed by the oxygen that was formerly thought to be adsorbed at the lower temperatures, so the interpretation must be correspondingly modified.

Finally, examples are occasionally found of surfaces on which the gases combine at velocities given by

$$\frac{dx}{dt} = kp_{\mathrm{H}_2}^2 \times p_{\mathrm{O}_2}.$$

Bodenstein‡ passed the mixed gases at atmospheric pressure and at 500–600° through porcelain reaction vessels of various surface/volume ratios. The results showed that the rates varied directly with the relative surface areas when the other factors were kept constant. It was therefore concluded that the reaction occurred exclusively on the surface. Furthermore, the variation of flow velocities and hydrogen/oxygen ratios indicated a third-order reaction which could be expressed by the above equation. But in the light of later work it is difficult to decide how much the gas phase reaction may have been contributing to the observed change, for the employment of static methods with porcelain reaction vessels has shown§ that the gas phase reaction occurs rather readily in this temperature range, and that the surface reaction obeys a first-order expression in agreement with the work of Bone and Wheeler.

A third-order mechanism is found|| when the reaction occurs on a gold surface at temperatures lower than those

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† Benton, *Trans. Faraday Soc.*, 1932, **28**, 215.

‡ Bodenstein, *Z. physikal. Chem.*, 1899, **29**, 665.

§ Gibson and Hinshelwood, *Proc. Roy. Soc.*, 1928, A, **119**, 591.

|| Benton and Elgin, *J. Amer. Chem. Soc.*, 1927, **49**, 2426.

used by Bone and Wheeler. The water formed by the reactants is strongly adsorbed on gold and therefore exerts an inhibiting influence by displacing hydrogen and oxygen. The kinetic expression is

$$dx \qquad k\,p^2_{\mathrm{H_2}}$$

Benton and Elgin concluded that a three-body surface collision led to reaction, and attributed the difference from the results of Bone and Wheeler to the different temperatures employed.

A study of the behaviour of atoms and radicals on various surfaces has been made by Taylor and Lavin.† Hydrogen atoms and free hydroxyl radicals were generated in a discharge tube and directed against thermometers whose bulbs had been coated with different catalytic materials. The subsequent temperature increases varied roughly with the ability of the coated bulbs to promote the recombination of the particles impingeing on them.

The reaction $H+OH \rightarrow H_2O$ was found to proceed most rapidly on such surfaces as alumina, which is a typical dehydration catalyst. Potassium chloride was less efficient but much better than clean glass surfaces.

For the reaction $H+H \rightarrow H_2$ the metals and such mixed oxides as $ZnO.Cr_2O_3$ gave the best results. All these substances are excellent dehydrogenation catalysts. Alumina was very inefficient and potassium chloride was almost as poor as clean glass.

It seems probable that these atom and radical recombinations are of great importance in initiating and breaking gas phase reaction chains. This point will be considered further in the chapters devoted to the homogeneous processes.

It should be stated here that the reaction occurring on a silica surface[†] is of the type where the rate varies directly as the pressure of hydrogen and is independent of the pressure of oxygen over a considerable range. Inasmuch as many of the investigations of the gas reaction were made with reaction vessels of silica, this relation should be remembered when dealing with the question of reaction chains which are affected by the nature of the wall.

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† Taylor and Lavin, ibid., 1930, **52**, 1910.

[†] Garstang and Hinshelwood, *Proc. Roy. Soc.*, 1931, A, **134**, 1.

III

THE PHOTOCHEMICAL REACTION

Photochemical observations are of importance in many investigations because of the precise knowledge which can be obtained of the primary processes of light absorption, and when there is a subsequent chemical change quantitative correlation of the primary and the ensuing processes becomes possible. Absorption can be measured without great experimental difficulty, the chief requirements being a monochromatic light source and some form of actinometer or thermopile to indicate the number of light quanta absorbed by the reacting system in unit time. The Stark-Einstein law of photochemical equivalence tells us that every such absorbed quantum excites one molecule to a point where chemical change may occur. Whether a subsequent reaction takes place depends upon a large number of factors, for the absorbed energy may be re-emitted as fluorescence or lost by collisions with other molecules. Such collisions may in turn result in the decomposition of the energy acceptor, or may merely cause a more equitable sharing of the energy without any accompanying decomposition. Sometimes, however, absorption leads directly to the decomposition of the absorbing molecule. To understand what will happen we require knowledge of the chemistry of the system as well as of its absorbing properties. But knowing the step which follows the initial absorption of the quantum, we are able to analyse what occurs, in a way which would be impossible without the aid of photochemistry, for we can now estimate the rate of formation of the initial products directly from their necessary equivalence with the amount of light absorbed.

More important still is the fact that, from the nature of the absorption spectrum, we can tell whether the primary effect of the light is to give rise to an excited molecule or to cause the splitting of the molecule of the absorbing substance into free atoms or radicals.

Thus, by employing suitable radiation, atoms of hydrogen and oxygen can be introduced at known rates into a reaction system. The direct formation of atoms from the hydrogen molecule by illumination with ultra-violet light is a matter of great experimental difficulty, owing to the extremely short wave-lengths needed. Although the dissociation requires only 101,000 calories per gram molecule, the necessity for an accompanying electronic excitation makes the desired result impossible to attain without using light in the almost inaccessible region of the ultra-violet. Oxygen, on the other hand, undergoes dissociation into atoms at about 1,700 Å., a region which can be investigated with the use of the aluminium spark.

Experiments in this region were made by Kistiakowsky,† who showed that the atoms so produced led to the formation of hydrogen peroxide when hydrogen was present. The following series of reactions was assumed to occur.

(1) $O_2+h\nu = 2O$

(2) $O+H_2 = OH+H$

(3) $H+O_2 = HO_2$

(4) $HO_2+H_2 = H_2O_2+H$

(5) $2OH = H_2O_2$ (three-body collision)

(6) $H+H = H_2$ („ „)

A good many hypotheses seem to be made in establishing a mechanism of this sort, so that it will be well to examine the reasons for assuming each successive step. The first reaction is known to occur from direct experimental evidence, oxygen atoms being detectable spectroscopically when quanta of such short wave-length are absorbed by the mixture. The oxygen atoms produced will presumably react with hydrogen molecules when they strike them.

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† *J. Amer. Chem. Soc.*, 1930, **52**, 1868.

Two possibilities now arise, namely the direct formation of water, or the production of free hydroxyl and a hydrogen atom. The former process is excluded on two grounds: first that it would not be in agreement with the experimental fact that hydrogen peroxide is practically the only end-product obtained, and again because of the difficulty of such an association reaction in the absence of a third body to dissipate the energy evolved. The alternative reaction $O+H_2 = OH+H$ is preferred because it is not only thermochemically possible, but will proceed by two-body collisions rather than require three-body collisions. The subsequent behaviour of the hydrogen atom assumed to be formed at this step must conform to the possibility of a continued chain of reactions, and must lead to the formation of hydrogen peroxide. When it strikes an oxygen molecule the two possibilities are the formation of $OH+O$, or step (3) of the scheme given. The former reaction is decidedly endothermic, and thus has a very small probability, particularly at low temperatures. The reaction (3) apparently needs a third body, a requirement which will be discussed later, but is exothermic, and plausible on structural grounds, if we remember that one of the two unpaired oxygen electrons is available to make the link with the hydrogen atom. The product HO_2 can then react as shown in step (4), with regeneration of a hydrogen atom, so that a continued chain is possible, and hydrogen peroxide is the only product of the cycle. The free hydroxyls formed in the second step can recombine to form additional hydrogen peroxide. Kistiakowsky's measurements showed that reaction (2) occurs only once in every 10^4 collisions, an interesting result in view of the fact that Polanyi has found almost perfect efficiency for several exothermic atom interchanges of this type. The chains produced by the repetition of (3) and (4) are of very short length, and, at room temperature, not more than about two molecules of hydrogen peroxide are formed per quantum of absorbed light. At higher temperatures the yields increase more rapidly than corresponds to the usual Arrhenius equation for change in reaction velocity with temperature, indicating an increase in the chain length. The low probability of reaction (2) has been verified in the direct experiments of Harteck and Kopsch,† who dissociated oxygen molecules by a discharge and passed the atom-rich mixture into molecular hydrogen. They found that the mixture reacted very slowly, so slowly indeed as to be practically outside the range of accurate measurement, because of the simultaneous occurrence of recombination of the oxygen atoms.

In addition to the method adopted by Kistiakowsky, there is another possible mode of photochemical investigation. This involves the use of substances known as 'sensitizers', which are capable of absorbing the incident radiation to give an excited molecule. This can then pass on the energy of excitation to the hydrogen, or the oxygen, of the mixture by means of inelastic collisions. Under these conditions the molecule receiving the impact is split into atoms which can form the nuclei of further reaction chains.

The most important example is mercury vapour, which can absorb the resonance radiation from a mercury lamp ($\lambda = 2{,}537$ Å.) by changing from the ^1S to the $^3P_1$ level. Collision of this excited atom with other mercury atoms or with inert gases results in a slight degradation to the metastable $^3P_0$ state, which contains excess energy corresponding to 107,000 calories per gram atom. It is not surprising that the subsequent collision of such an excited atom with a molecule of hydrogen (heat of dissociation 101,000 cal.) should result in the decomposition of the latter into atoms, whereas oxygen molecules (heat of dissociation 117,000 cal.) absorb the energy to give excited molecules rather than oxygen atoms.

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† *Z. Elektrochem.*, 1930, 36, 714.

The discovery of this process by Cario and Franck† was followed by the work of Marshall,‡ who found that the absorption of the 2,537 Å. line by a mixture of hydrogen and oxygen containing mercury vapour led to the production of hydrogen peroxide rather than water. The yield was variable, the average being about 2·5 molecules for each quantum of absorbed light. The mechanism suggested by Marshall‡ was similar to that adopted later by Kistiakowsky in his explanation of the non-sensitized reaction, except that the initial step is the production of hydrogen rather than oxygen atoms.

$$\begin{aligned} &(1) & \mathrm{Hg}+h\nu &= \mathrm{Hg}^* \\ &(2) & \mathrm{Hg}^*+\mathrm{H}_2 &= \mathrm{Hg}+2\mathrm{H} \\ &(3) & \mathrm{H}+\mathrm{O}_2 &= \mathrm{HO}_2 \\ &(4) & \mathrm{HO}_2+\mathrm{H}_2 &= \mathrm{H}_2\mathrm{O}_2+\mathrm{H} \\ &(5) & \mathrm{H}+\mathrm{H} &= \mathrm{H}_2 \text{ (three-body collision).} \end{aligned}$$

The third step is exothermic. The fourth is endothermic and will therefore have a low efficiency and lead only to short chains. If it were highly efficient (3) and (4) could be repeated to give much longer chains. The mechanism satisfies the chief experimental requirements, low quantum yields and the almost exclusive formation of hydrogen peroxide.

Frankenburger and Klinkhardt§ made further investigations between 50° and 200° C. and at 1 to 11 atmospheres pressure and found about one molecule of hydrogen peroxide and two molecules of water for each quantum absorbed. They objected to the Marshall chain on the ground of the lack of spectroscopic evidence for the existence of HO_2, the endothermicity of step (4)—supposed at the time to be –31,000 cal.—and on account of the necessity for explaining the formation of water in addition to hydrogen peroxide. They adopted the Haber mechanism which had been postulated to explain the burning of hydrogen-oxygen mixtures at much higher temperatures. The essential reactions are

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† Cario and Franck, *Z. Physik*, 1922, **21**, 161.

‡ Marshall, *J. Phys. Chem.*, 1926, **30**, 34, 1078; *J. Amer. Chem. Soc.*, 1932, **54**, 4460.

§ Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, 1931, **27**, 431.

$$(1)\quad H+O_2+H_2 = H_2O+OH$$
$$(2a)\quad OH+H_2 = H_2O+H$$
$$(2b)\quad 2OH = H_2O_2 \text{ (three-body collision).}$$

The first step has a rather closer relation to the corresponding link in the chain suggested by Marshall than might at first appear. If we consider the step represented formally by a three-body collision to be actually a pair of two-body collisions following one another in rapid succession, we can split the first step thus:

$$(1a)\quad H+O_2 = HO_2^*$$
$$(1b)\quad HO_2^*+H_2 = H_2O+OH.$$

(The asterisk indicates an activated molecule.)

Leaving until later a discussion of the nature of HO_2^* we can see that Haber's scheme differs from Marshall's solely in the production of H_2O and OH in place of H_2O_2 and H.

From an analysis of the reaction kinetics, Frankenburger and Klinkhardt concluded that step (2a), although exothermic, was relatively inefficient at low temperatures and would require an activation energy of at least 14,000 calories. This means that practically all the hydroxyls are used up in (2b). On this basis it is found that each absorbed quantum gives two hydrogen atoms, which will lead to the formation of one molecule of hydrogen peroxide and two of water, in fair agreement with experiment. To explain the occasional formation of more than one molecule of hydrogen peroxide per quantum it was assumed that the following step

$$H+O_2+H_2O = H_2O_2+OH$$

can sometimes occur, resulting in a yield of $3H_2O_2$ and no water per quantum. These conclusions were not without their difficulties. Step (2b) was held by Bonhoeffer and Pearson[†] to be a relatively unimportant process compared with

$$OH+OH = H_2O+O.$$

The doubts cast upon the reality of HO_2 have been weakened by its detection in the mass spectrograph (Eisenhuth). Furthermore, the chain-producing step in Marshall's scheme,

$$HO_2+H_2 = H_2O_2+H,$$

which was formerly thought to be endothermic to the extent of 31,000 cal., now appears to be more nearly thermoneutral. It should also be remembered that the HO_2 molecule may often carry its original energy of formation into the next step, and so give a definitely exothermic reaction.

We must now consider some experiments which seem to allow a definite decision to be made between the two mechanisms. Bates and Salley[‡] showed that the illumination of a carefully dried mixture of hydrogen and oxygen containing mercury vapour gave a product containing more than 80 per cent. of hydrogen peroxide, the value rising to 88 per cent. under particularly favourable conditions. They concluded that the only primary product is hydrogen peroxide and that water is a secondary product arising from the decomposition of this peroxide. The Haber scheme predicts a maximum of 48 per cent. by weight of hydrogen peroxide and thus seems to be definitely excluded from the low-temperature, mercury-sensitized reaction.

The HO_2 mechanism has received further but more indirect support from the work of Bates and Lavin[§] on

[†] Bonhoeffer and Pearson, *Z. physikal. Chem.*, 1931, B, **14**, 1.

[‡] Bates and Salley, *J. Amer. Chem. Soc.*, 1933, **55**, 110.

[§] Bates and Lavin, ibid., 1933, **55**, 81.

the photochemical oxidation of hydrogen iodide. The first step in this reaction is the splitting of hydrogen iodide into atoms.

$$(1)\quad HI+h\nu = H+I.$$

This step is followed by

$$\begin{aligned}
(2)&\quad H+HI = H_2+I\\
(3)&\quad H+O_2 = HO_2\\
(4)&\quad HO_2+HI = H_2O_2+I\\
(5)&\quad HO_2 = H+O_2.
\end{aligned}$$

The hydrogen peroxide is not always isolated, because of its rapid decomposition to water and oxygen in the presence of iodides. From the relative amounts of water, hydrogen, and iodine formed under varying conditions of pressure and light intensity, the relative values of the different velocity constants in the above reaction scheme can be inferred. Bates and Lavin argue that since the velocity constants of (2) and (3) appear to bear a fixed ratio to one another, the reversal of (3) by (5) must take place to a limited extent only, an upper limit of $k = 10^9$ being fixed for (5). This means that HO_2 is a far more stable compound than might have been thought, the calculated mean life being of the order of 10^{-8} or 10^{-9} rather than the usual 10^{-13} seconds.

Bates adopts the Marshall scheme for the photosensitized combination of hydrogen and oxygen, except that he assumes chain breaking to be due chiefly to the reaction of two HO_2 molecules, the concentration of HO_2 now being assumed to be appreciable on the basis of the considerations just referred to.

An investigation of Bodenstein's† on the photochemical behaviour of mixtures of oxygen, hydrogen, and chlorine must now be considered. It is well known that illumination of hydrogen-chlorine mixtures gives rise to the so-called Nernst chain, lately reinstated in scientific favour after a period of discredit.

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† Bodenstein and Schenk, *Z. physikal. Chem.*, 1933, B, **20**, 420.

$$\begin{aligned} Cl_2+h\nu &= 2Cl \\ Cl+H_2 &= HCl+H \\ H+Cl_2 &= HCl+Cl. \end{aligned}$$

Such chains are very sensitive to traces of oxygen, and it has been found, by varying the hydrogen/chlorine ratio, that they are chiefly broken by the interaction of hydrogen atoms with molecules of oxygen. Bodenstein and Schenk investigated the dependence of the yield of water on the relative proportions of hydrogen, chlorine, and oxygen. To explain the results they postulate the step $H+O_2 = HO_2$ followed by one of three possibilities:

$$(1)\ HO_2+HCl = H_2O+ClO, \quad (2)\ HO_2+Cl_2 = HCl+ClO_2,$$
$$(3)\ HO_2+H_2 = H_2O+OH.$$

Each one of these three possibilities in turn leads to a series of reactions which can be made to explain the experimental results. To avoid making (1) and (2) endothermic it is necessary to give HO_2 a heat of formation with an upper limit of 44,000 calories, which is considerably less than the usual estimate. Bodenstein estimates† the lower limit to be 38,000, and the most probable value to be about 40,000. As already stated, this leads to a new value of about –2,000 cal. instead of –31,000 for the step $HO_2+H_2 = H_2O_2+H$. Furthermore, by considering the numerical values of various velocity constants, Bodenstein and Schenk show that at 300 mm. total pressure the bimolecular reaction $H+O_2 = HO_2$ has $k = 3\times10^3$ mm./min., which corresponds to a very high efficiency of the three-body process $H+O_2+M = HO_2+M^*$, where M is any third molecule.

† The lower limit was estimated in the following way. For reasons given on page 22 Bodenstein rejects the step $HO_2+H_2 = H_2O_2+H$ in favour of the variation $HO_2+H_2 = H_2O+OH$. Assuming that it does not occur, he infers that the former process is improbable on thermal grounds. To make the step endothermic HO_2 must be given a heat of formation greater than 38,000 calories.

But having confirmed the work of Bates and Lavin to the extent of showing the stability of HO_2, and determining a heat of formation of such a value as to increase the probability of the reaction

$$HO_2+H_2 = H_2O_2+H,$$

Bodenstein points out a serious difficulty. His experiments show that a chain is broken every time an HO_2 molecule is formed, and that the subsequent career of the HO_2 must finally end in the production of H_2O without forming new chains. The hydrogen atom liberated in the above reaction should start a fresh Nernst chain, a possibility which is excluded by the quantum yield of water found experimentally. As a result the Haber mechanism in a modified form is used to explain the chain breaking.

$$\begin{aligned} M+H+O_2 &= HO_2+M \\ HO_2+H_2 &= H_2O+OH \\ OH+Cl &= HCl+O \\ O+2HCl &= H_2O+Cl_2. \end{aligned}$$

The various reaction mechanisms proposed for hydrogen-oxygen mixtures have been compared by Bates,† who estimates the values of the velocity constants of the different steps, and considers predictions made from the theoretical mechanisms in the light of the collected experimental results. The original chain proposed by Marshall predicts the formation of hydrogen peroxide and the quantum yields in a satisfactory manner, but fails to explain the dependence of the yields on the concentration of hydrogen and oxygen.

The Haber-Frankenburger-Klinkhardt mechanism predicts the right sort of quantum yield, but will give high yields of hydrogen peroxide only if the reaction

$$HO_2+H_2O = H_2O_2+OH$$

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† *J. Chem. Physics*, 1933, **1**, 457.

is assumed to be about five thousand times as rapid as

$$HO_2+H_2 = H_2O+OH.$$

If this necessary assumption is made, it is found that a difficulty arises in that the expected variation of the rate with added water vapour is not found. Finally, Bates's own modification of the Marshall theory is shown to yield nothing but hydrogen peroxide, as experiment requires, and to give fair agreement with the observed quantum yields, temperature coefficient, and effect of hydrogen-oxygen ratios. The predicted effect of varying the light intensity is in less accurate agreement with observation.

On the whole it must be concluded that a quite definite decision is difficult to make, but that there is a good deal in favour of the Marshall-Bates mechanism.

Other substances besides mercury have a sensitizing effect in the photochemical reaction. The action of nitrogen peroxide will be discussed elsewhere in connexion with the thermal reaction of the same system.

Farkas, Haber, and Harteck† have used ammonia as a photochemical sensitizer, the primary process being

$$NH_3+h\nu = NH_2+H,$$

according to Bonhoeffer.‡ The light source was a condensed zinc spark. They found that explosions of hydrogen-oxygen mixtures occurred above 415° and 300 mm. pressure, if the system contained small amounts of ammonia.

The explosions usually followed induction periods of varying length. The results were interpreted on the basis of the Haber chain, the transition from steady reaction to explosion being presumed to correspond to the substitution of the step

$$H+O_2+H_2 = 2OH+H-10{,}000 \text{ cal.}$$

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† *Z. Elektrochem.*, 1930, **36**, 711.

‡ Bonhoeffer and Farkas, *Z. physikal. Chem.*, 1928, **132**, 235.

for the one assumed at lower temperatures,

$$H+O_2+H_2 = OH+H_2O+102{,}000 \text{ cal.}$$

Other sensitizers were also used, such as hydrogen sulphide, sulphur dioxide, and oxides of nitrogen. In the latter case oxygen atoms were supposed to be the primary product of light absorption, the reaction continuing through the process

$$O+H_2 = OH+H+3{,}000 \text{ cal.}$$

It was shown by Taylor and Salley,† however, that the chain length varied with the concentration of ammonia, a maximum being quickly reached at relatively low concentration, and further addition of ammonia shortening the chain once more. It is obvious, therefore, that besides starting the chain the ammonia must take part in the various links in some way. Thus a chain mechanism of greater complexity than a simple Haber chain initiated by hydrogen atoms must be assumed.

To summarize the conclusions which can be drawn from the photochemical work, it may be said that while the interpretation of the results is by no means final, a few generalizations of high probability may be made. In the photochemical reaction at low temperatures we can say that excited mercury atoms cause the splitting of hydrogen molecules into atoms, and that the most probable fate of these is that they should meet and combine with oxygen molecules giving the molecule HO_2. When relieved of its energy of formation this molecule can probably exist for something like 10^{-8} seconds on the average, which allows it to suffer many collisions before losing its identity. Since the evidence points to the ultimate formation of hydrogen peroxide to the exclusion of other products, the most probable step in the subsequent transformation seems to be $HO_2+H_2 = H_2O_2+H$. This reaction, being endothermic, will not give rise to long chains, but it is not endothermic enough for its probability to be vanishingly small. This is in harmony with the experimental fact that the quantum yield of hydrogen peroxide is usually about two.

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† Taylor and Salley, *J. Amer. Chem. Soc.*, 1933, 55, 96.

The unsensitized photochemical reaction must proceed from the initial formation of oxygen atoms, the next step being presumably the rather inefficient $O+H_2 = OH+H$. The subsequent reactions will involve polymerization of the free hydroxyls, while the hydrogen atoms will either recombine or furnish hydrogen peroxide through the same series of steps as in the mercury-sensitized reaction. Apart from the first step, then, the mechanism is probably similar in the two processes.

It must be remembered that the conditions of the photochemical observations are quite different from those of the thermal reaction at higher temperatures. Thus conclusions about the mechanism of one type of reaction may not be at all applicable to the other. However, observations on the variation of the photochemical chain length with temperature are of importance in bringing the two mechanisms into relation with one another. Kistiakowsky† showed that the temperature coefficient of the direct photochemical reaction was about 1·05 for ten degrees at room temperatures, but increased to 1·25 in the neighbourhood of 500°. He concluded that this corresponded to a lengthening of the chains. Taylor and Salley found a similar increase in the temperature coefficient of the mercury-sensitized reaction, the increase occurring rather sharply at about 490°. The results should be borne in mind when the relation of the thermal and photochemical mechanisms is discussed.

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† Kistiakowsky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 194.

IV

ENERGY CONSIDERATIONS

In order to decide whether a given reaction involved in a chain is probable or not it is necessary to know the corresponding heat change, for a step involving a large absorption of energy could only occur rarely when the necessary energy of activation was available.

The quantities which are given below represent the changes in heat content when the reactions are carried out at the absolute zero. They can be used as a first approximation for our present purposes.

$H+H \rightarrow H_2$

The first measurements are due to Langmuir,† who investigated the conductivity of heat from an incandescent tungsten wire through an atmosphere of hydrogen. His earlier results gave a value of 136,000 calories for the heat evolved in the above process, later refinements changing the value to about 90,000. The method is essentially only an approximate one.

The earlier spectroscopic determinations of the dissociation energy gave results as low as 74,000 calories,‡ but by extrapolation of vibrational levels obtained from band spectra the calculations finally yielded values close to 100,000 calories.§ Subsequent refinements have been of a minor nature, and the spectroscopic results|| are now in very close agreement with those obtained by electron bombardments.†† We shall adopt 101,000 as the final value.

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† Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 860; 1915, **37**, 417.

‡ Mohler and Foote, *J. Optical Soc. Amer.*, 1920, **4**, 49.

§ Witmer, *Phys. Rev.*, 1926, **28**, 1223.

|| Birge, *Nature*, 1928, **121**, 134; Richardson and Davidson, *Proc. Roy. Soc.*, 1929, A, **123**, 483.

†† Lozier, *Phys. Rev.*, 1933, **44**, 575.

$O+O \rightarrow O_2$

By investigation of the vibrational bands of oxygen, Birge and Sponer[†] obtained a value of 162,000 cal. for this process. A variety of methods,[‡] such as predissociation, spectrum analysis, ozone decomposition, and thermal conductivity gave results which were generally lower and showed poor agreement with one another. The spectral difficulties were removed when it was realized that the original calculations had failed to consider the excitation energy of one of the resultant oxygen atoms, which appeared in the ^1D state. Frerichs[§] showed that this state was 45,000 calories above the normal, and when this correction is introduced we obtain 117,000 as the value that is now accepted. Herzberg[||] has shown that Frerichs's results also account for the deviations obtained when predissociation methods are used.

$H+OH \rightarrow H_2O$

The equilibrium of this process has been measured thermally near 1,200° C. by means of the absorption spectrum of OH, and the change of equilibrium with temperature gives a value of $115{,}000 \pm 5{,}000$ calories for the heat of reaction.[††]

Investigation of the ultra-violet absorption spectrum of steam[‡‡] gives 112,000, which is in very close agreement with the value found by means of the following mercury-sensitized process:[§§]

$$Hg'+H_2O \rightarrow HgH+OH.$$

[†] Birge and Sponer, *Phys. Rev.*, 1926, **28**, 259.

[‡] Kassel, *Phys. Rev.*, 1929, **34**, 817; Henri, *Compt. Rend.*, 1930, **190**, 179; Henri, *Nature*, 1930, **125**, 275; Jenkel, *Z. physikal. Chem.*, 1931, **155**, 100.

[§] Frerichs, *Phys. Rev.*, 1930, **36**, 398.

[||] Herzberg, *Z. physikal. Chem.*, 1930, B, **10**, 189.

[††] Bonhoeffer and Reichardt, *Z. Elektrochem.*, 1928, **34**, 652.

[‡‡] Leifson, *Astrophys. Journ.*, 1926, **63**, 73; Mecke, *Z. Physik*, 1932, **33**, 1.

[§§] Senftleben and Rehren, *Z. Physik*, 1926, **37**, 526.

We shall adopt 112,000 as the most probable value.

This well-investigated process yields about 57,000 cal. at 0° abs.[†]

$H_2+O_2 \rightarrow H_2O_2$

The thermal changes of this process can be found with the help of the reaction $H_2O_2 \rightarrow H_2O+\frac{1}{2}O_2$ and the use of Hess's law. As given above it is about 38,000 calories exothermic.[‡]

We may summarize the values so far obtained. The accuracy is such that all thermal values deduced from them should be correct within a few thousand calories. Water and hydrogen peroxide have been calculated as gases.

Direct measurements have given

$$\begin{aligned} H+H &\rightarrow H_2+101{,}000, \\ O+O &\rightarrow O_2+117{,}000, \\ H+OH &\rightarrow H_2O+112{,}000, \\ H_2+\tfrac{1}{2}O_2 &\rightarrow H_2O+57{,}000, \\ H_2+O_2 &\rightarrow H_2O_2+38{,}000. \end{aligned}$$

These lead to the following values:

(*a*) For the formation of hydrogen peroxide

$$\begin{aligned} H+H+O+O &\rightarrow H_2O_2+256{,}000, \\ H+H+O_2 &\rightarrow H_2O_2+139{,}000. \end{aligned}$$

(*b*) For the formation of water and of hydroxyl

$$\begin{aligned} O+H &\rightarrow OH+104{,}000, \\ H+H+O &\rightarrow H_2O+216{,}000. \end{aligned}$$

(*c*) For the formation of HO_2

$$\begin{aligned} H+O+O &\rightarrow HO_2+157{,}000, \\ H+O_2 &\rightarrow HO_2+40{,}000, \end{aligned}$$

[†] Lewis, *J. Amer. Chem. Soc.*, 1914, **36**, 1969.

[‡] von Wartenberg and Sieg, *Ber.*, 1920, **53**, 2192.

assuming the conclusions of Bodenstein and Schenk (see previous chapter), but if we assume equality of the H—O links in H_2O_2 we have

$$H+O_2 \rightarrow HO_2+69{,}500,$$

$$HO_2+H \rightarrow H_2O_2+69{,}500.$$

Finally, we have for the essential processes of the Haber and Bates-Marshall chains

$$H+O_2+H_2 \rightarrow H_2O+OH+102{,}000,$$

$$OH+H_2 \rightarrow H_2O+H+11{,}000.$$

If we assume the Bodenstein-Schenk value for the process $H+O_2 \rightarrow HO_2$ we have

$$H+O_2 \rightarrow HO_2+40{,}000,$$

$$HO_2+H_2 \rightarrow H_2O_2+H-2{,}000.$$

If the HO_2 is supposed to carry its energy of formation into the next step without loss we eliminate all energy uncertainties and obtain

$$H+O_2+H_2 \rightarrow H_2O_2+H+38{,}000.$$

THE GASEOUS REACTION AT HIGHER PRESSURES

At temperatures below, or not much above 500° C. the combination of hydrogen and oxygen in the absence of ultra-violet light takes place almost entirely on the walls of the containing vessel. When the latter is of silica or porcelain the reaction is approximately of the first order, has a small temperature coefficient, and is retarded by steam, which acts as a 'catalytic poison' to the surface. With a silica vessel, as was shown in an earlier chapter, the rate is directly proportional to the pressure of hydrogen and almost independent of the oxygen concentration, except at low partial pressures. The reaction is in fact a typical heterogeneous one.

At high temperatures a mixture of oxygen and hydrogen explodes, and there can be no doubt that the explosion is a homogeneous reaction, at any rate as far as its propagation is concerned, whatever the mode of initiation may be. The idea arose of investigating carefully the behaviour of the system in a region of temperature extending right up to the explosion point, to see whether any homogeneous reaction of measurable speed appeared. Between 540° and 600° rather remarkable phenomena are met with.†

Between two definite limits of pressure the gases inflame as soon as they are mixed. But there is a limiting pressure of either gas above which the second gas may be added to it without ignition occurring. The upper pressure limit varies with temperature, but is not very high, being, for example, at 550° of the order of 100 mm. This phenomenon can be observed at as low a temperature as 460°. It may be called the 'low-pressure explosion' phenomenon,

† Hinshelwood and Thompson, *Proc. Roy. Soc.*, 1928, A, **118**, 170; Gibson and Hinshelwood, ibid., 1928, A, **119**, 591.

and is discussed in detail in the next chapter. The present chapter deals with the reaction occurring when the pressures of hydrogen and oxygen are above the upper limit of the low-pressure explosion region.

At 540° in a silica bulb of about 250 c.c. capacity 50 mm. of oxygen could be admitted to 100 mm. hydrogen, and the rate of reaction followed by observing the pressure changes.

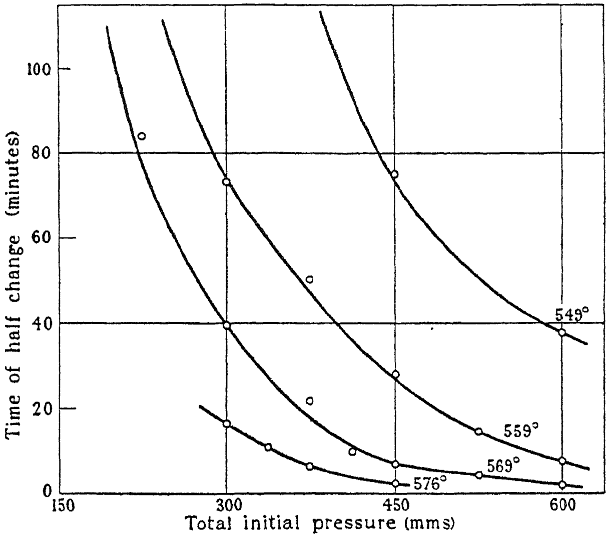

Fig. 1.

The rate would be very small. But it would increase rapidly as the initial pressures were raised, the reaction being of a 'high order'. The order of the reaction increases with the temperature, and presently attains a value of about four. But this number varies with the conditions somewhat.

The diagram shows the influence of the initial pressure on the rate of reaction at various temperatures. The experiments were made in a porcelain vessel. What is actually plotted is the time for half the original gas to combine. This time is of course an inverse measure of the rate of reaction.

The concentration of hydrogen influences the rate more than that of the oxygen. In a porcelain vessel at 569° the

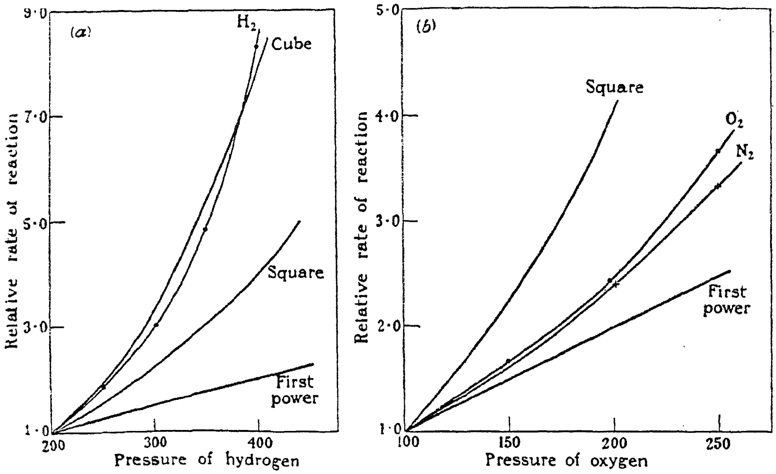

FIG. 2.

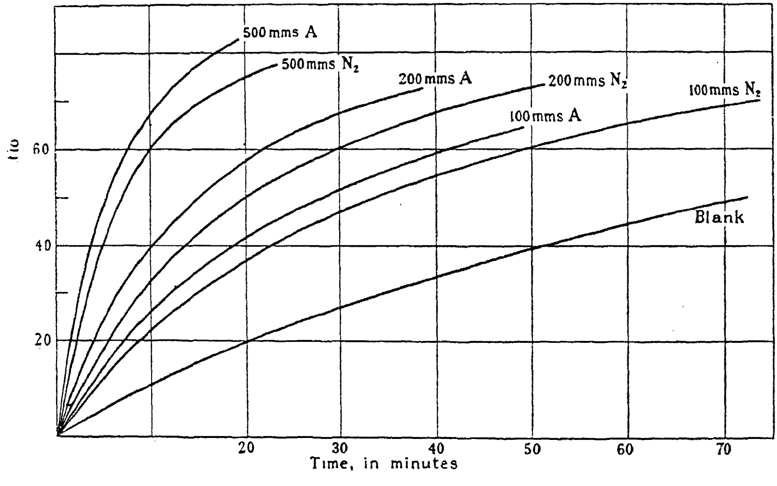

FIG. 3.

rate was found to be approximately proportional to the cube of the partial pressure of hydrogen, and proportional to a power of the oxygen concentration between the first and the second. In a silica vessel at 549° the rate varied roughly as more than the square of the hydrogen pressure and about as the first power of the oxygen pressure. The pressure influence is further shown in Fig. 2.

The reaction in the region of temperature and pressure considered is autocatalytic, the speed increasing quite markedly as steam accumulates in the vessel. This is in sharp contrast with the surface reaction prevailing at lower temperatures, which is 'poisoned' by steam. The autocatalytic effect is shown in the following table.

Bulb 1. 549°. 403 mm. H_2; 212 mm. O_2			Bulb 2. 533°. 401 mm. H_2; 197 mm. O_2		
t	x	Δt (for 5 mm.)	t	x	Δt (for 10 mm.)
0	0		0	0	
36″	5	36″	4′ 55″	10	4′ 55″
1′ 2″	10	26″	8′ 2″	20	3′ 7″
1′ 27″	15	25″	10′ 25″	30	2′ 23″
1′ 54″	20	27″	12′ 50″	40	2′ 25″
2′ 15″	25	21″	14′ 52″	50	2′ 2″
2′ 38″	30	23″	17′ 20″	60	2′ 28″
2′ 56″	35	18″	19′ 13″	70	1′ 53″
3′ 18″	40	22″	21′ 10″	80	1′ 57″
3′ 35″	45	17″	23′ 10″	90	2′ 0″
3′ 54″	50	19″	26′ 5″	100	2′ 55″
4′ 30″	60	2×18″	31′ 50″	120	2×2′ 53″
5′ 3″	70	2×16·5″	41′ 0″	143	
6′ 11″	90	4×17″	58′ 30″	165	
6′ 48″	100	2×18·5″	107′ 0″	185	
7′ 30″	110	2×21″	120′ 0″	190	
8′ 19″	120	2×24·5″	130′ 0″	192	
10′ 17″	140	4×29·5″	∞ (calc.)	197	
11′ 50″	150	2×46·5″			
13′ 55″	160	2×62·5″			
17′ 18″	170	2×1′ 41″			
23′ 4″	180	2×2′ 53″			
33′ 15″	190	2×5′ 5″			
∞ (calc.)	201·5				

The accelerating action of steam proves, however, to have no specific chemical significance, since other foreign gases have similar accelerating influences and steam merely falls into its place among other 'inert gases' such as helium, argon, or nitrogen. The influence of these is very marked and is illustrated in Fig. 3.

The initial rate of reaction, for a given pressure of hydrogen and oxygen, increases rather more than in linear proportion to the inert gas concentration, but up to about 400 mm. of the inert gas a linear relationship represents the facts sufficiently well. Taking a considerable number of measurements into account, the following order was arrived at for the relative influences of the different gases:

$$\mathrm{He : N_2 : A : H_2O :: 1 : 3 : 4 : 5.}$$

With regard to the absolute magnitude of the effect Fig. 2 shows that the addition of nitrogen produces approximately the same increase in rate as an increase in the oxygen concentration by an equal amount would have done. The following numbers show the approximately linear increase in rate with addition of nitrogen, at any rate for the first additions:

Pressure of hydrogen 200 mm.; pressure of oxygen 100 mm.
Temperature 559°

Pressure of nitrogen in mm.	Rate relative to rate in absence of nitrogen	
	obs.	calc. $(1+0{\cdot}013\ N_2)$
0	1·00	1·00
100	2·23	2·30
200	3·64	3·60
300	4·61	4·90
500	10·4	7·5

The nature of the 'inert gas effect' is revealed by a study of the influence of the vessel diameter on the rate of reaction.

This effect is very great indeed. As an example the following may be quoted. Two silica bulbs were constructed, identical in all respects except that one contained 17 lengths of silica tubing as packing. The volume of the unpacked bulb was 301 c.c., and its internal surface area was 256 sq. cm. The free volume of the packed bulb was 230 c.c. and its internal surface area was 1,245 sq. cm. The diameter of the packing tubes was 1 cm. At 550°, with an equivalent mixture of hydrogen and oxygen, the speed of reaction was 12·6 times greater in the unpacked bulb when the initial pressure was 600 mm., and 17·9 times greater when the initial pressure was 300 mm. By completely packing the vessel with small silica spheres the reaction can be almost inhibited except for the residual first-order surface reaction. The same result can be achieved by introducing powdered silica or porcelain into the reaction vessel, but this method is rather crude, since the increase in actual surface is so great that the extra heterogeneous reaction partly compensates for the diminished gas reaction. It is the reduction in the linear dimensions of the gas space which is the important factor in suppressing the gas reaction. Increase of surface, as such, is a less effective means of reducing the rate.

A quantitative relation between vessel diameter and reaction rate is not easy to establish with accuracy, since the nature and previous treatment of the surface, as well as the size of the vessel, exert their effect. A series of experiments made in a given vessel will exhibit a drift, the rate of reaction rising and falling as the state of the surface changes. These drifts are not serious enough to cast any doubt on the existence of the phenomena described, but merely make the discovery of exact quantitative rules difficult. Added to this is the fact that, simultaneously with the high-order reaction of which these various effects are characteristic, there is at the same time some purely heterogeneous reaction, the exact proportion of which is not easy to ascertain accurately on account of the variability of surface from experiment to experiment. Nevertheless it may be said that the nearest approximation to the truth is given by the statement that the rate is proportional to the square of the vessel diameter.

This is shown by the following experimental results.† Silica bulbs of varying diameters but identical lengths were employed as reaction vessels for mixtures of two parts of hydrogen to one of oxygen at 560°. Rates were measured for initial pressures of 300 mm. and of 600 mm. The differences between these rates were taken as quantities, which, for a given vessel, measured the speed of the homogeneous reaction and were less influenced by varying proportions of wall reaction. The average numerical values obtained were as follows:

Bulb diameter mm.	17	32	56	77
Rate, 600 mm.	0·85	3·49	9·35	33·8
Rate, 300 mm.	0·18	0·50	0·94	3·45
$(v_{600}-v_{300})/d^2$	0·00232	0·00292	0·00268	0·00512
$(v_{600}-v_{300})/d$	0·0394	0·0935	0·150	0·394

It is evident that a reasonable constant is obtained if we assume the rates to vary as the square of the diameters, the only abnormal results being found with the largest bulb. This, however, is understandable when it is remembered that the measurements made in this bulb were on the border-line of the explosion region. (This explosion is of the sort that occurs at high temperatures when the rate becomes too great, and is not to be confused with the low-pressure explosions discussed elsewhere.) If the rates are divided by the first power of the diameter no sort of constancy is obtained.

The explanation of these facts about the influence of the vessel size and the effect of inert gases on the reaction rate becomes quite simple if the hypothesis of reaction chains is adopted.

A reaction chain is a process in which an initial chemical transformation gives rise to an intermediate product of high chemical activity, capable of reacting with the other substances present and being regenerated in successive cycles of change. The following would be examples:

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† Williamson, Pickles, and Hinshelwood, unpublished results.

$$2H_2+O_2 = H_2O+H_2O^*$$

$$H+O_2 = HO_2 \qquad H_2O^*+O_2 = H_2O+O_2^*$$

$$HO_2+H_2 = H_2O_2+H \qquad O_2^*+2H_2 = H_2O+H_2O^*$$

where H_2O^* means an activated molecule of steam.

Such cycles would go on indefinitely unless the chain were broken by the deactivation or destruction of the active intermediate product. Their existence was first discovered by observation of the very high yield of chemically transformed molecules for each quantum of light absorbed in certain photochemical reactions.† The hydrogen-oxygen reaction was the first example of their appearance in a thermal gas reaction. Here we infer the existence of reaction chains in the following way. The breaking of the chain might occur by the destruction of the active intermediate or 'chain carrier' in the gas phase, or by its destruction or removal in a chemical reaction or physical deactivation process occurring at the surface of the containing vessel. The chain can only be broken at the wall of the vessel in so far as the chain carriers diffuse there. The greater the dimensions of the vessel the longer will be the time during which the carriers survive in the gas phase without destruction, and, in the course of this longer time, the greater will be the number of cycles of change run through. Thus the rate of reaction will increase with the size of the vessel. Similarly, when an inert gas is added to the system the rate of diffusion of chain carriers to the wall is impeded: a given chain traverses a zigzag path through the gas for a longer time, and during this time more chemical change takes place. Thus the inert gas has the same effect as an increase in the diameter of the vessel. (It must not be thought that the number of collisions made in the course of a chain is increased only to the extent of those in which the inert gas itself participates. On the contrary the inert gas increases the actual *time* taken for the chain to thread its way, in a kind of Brownian motion, to the wall, and thus increases the number of encounters between the kinds of molecule actually concerned in the reaction.)

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† See Clusius, 'Kettenreaktionen', *Fortschritte d. Chem., Phys. u. phys. Chem.*, 1932; Hinshelwood, *Kinetics*, Oxford, 1933, for references to the work of Nernst, Bodenstein, Christiansen, Bäckström, and others on chain processes in general.

Since in the hydrogen-oxygen combination we find precisely the effects to be anticipated for a reaction occurring by means of chains which traverse the gas and are broken at the wall of the vessel, and since no simple alternative explanation presents itself, we conclude that the two gases do in fact combine by such a chain mechanism.

The influence which the diameter of the vessel should have on the rate of the reaction can be calculated from the Einstein-Smoluchowsky equation† for the mean displacement of a particle executing a random motion. If the path of the particle were straight, its displacement would vary in direct proportion to the time; since, however, the motion is random and zigzag, the path is largely re-entrant, and the mean displacement increases less rapidly than the time. It varies in fact as the square root of the time. Conversely, the mean time required for a particle to diffuse a given distance from its original position varies as the square of that distance. The time is also inversely proportional to the coefficient of diffusion of the particles through the surrounding medium.

The number of links in a chain varies directly with the length of time for which the chain continues. For a given gas mixture, therefore, the length of a chain which is terminated only by the wall will vary as the square of the diameter of the vessel, since the chain length depends not upon the mean displacement but upon the total length of the zigzag path. Suppose we have a series of cylindrical vessels of the same length but different diameters. The total amount of chemical change is proportional to the chain length multiplied by the number of chains starting in unit time. The chain length depends upon the square of the diameter. If the chains start in the gas, the number is proportional to the volume of the vessel, while if they start at the wall of the vessel, the number is proportional to the area of the surface. In the first case the total amount of change is proportional to volume $\times$ (diameter)^2, and thus the velocity constant of the reaction, which depends upon the amount of change per unit volume, is proportional to the square of the diameter. In the second case the velocity constant will be proportional to (diameter)$^2 \times$ (surface area/volume). For the series of cylindrical vessels with a small diameter/length ratio, area/volume varies inversely as the diameter. Thus the velocity constant will vary as the first power of the diameter.

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† The first application of this equation to the quantitative treatment of chain reactions was made by Semenov in connexion with the oxidation of phosphorus, *Z. Physik*, 1927, **46**, 109.

There is no reason to suppose that the efficiency of the wall in breaking the chains which arrive there is unity. Some of the chains might be reflected. The 'coefficient of reflection' can depend upon the state of the surface, and in particular upon the nature of the adsorbed gas films. These, as is well known, are apt to vary in a way which is difficult to control. Hence there appears a certain variability in the results found with two apparently identical vessels. This makes an absolutely certain determination of the law connecting diameter and rate difficult to obtain. But the results quoted above point to the conclusion that, at least approximately, the rate varies as the square of the diameter. Thus the probability that the chains start in the gas phase rather than at the surface is considerable. It will be necessary to return to this subject again later.

The rate of reaction should be inversely proportional to the diffusion coefficient. The theory of the diffusion of one gas through a mixture of others is by no means simple. In the first place, the diffusion coefficient depends upon the molecular weight of the diffusing gas. Thus, in the present example, we need to know the mean molecular weight of the chain carriers. The Stefan-Maxwell theory gives the following formula for the diffusion coefficient of one gas into another:

$$D = \frac{1}{S_{12}^{2}}\sqrt{\left(\frac{1}{m_1} + \frac{}{m}\right.}$$

m_1 and m_2 are the molecular weights of the two gases, and S_{12} is the arithmetic mean of the diameters of the two kinds of molecules. The table[†] gives relative values of $1/D$ for different gases, assuming the various molecular weights for the chain carriers.

	Relative values of 1/(diffusion coefficient) (He = 1) for diffusion in					
m_2	H_2	He	N_2	O_2	A	H_2O
$H_2 = 2$	1·0	1·0	2·1	2·0	2·0	2·5
$H_2O = 18$	0·9	1·0	2·8	2·8	2·9	3·0
$H_2O_2 = 34$	0·9	1·0	2·9	2·9	3·05	2·95

When m_2 is about 18 the order of the $1/D$ values is the same as the observed accelerating influences of the various gases. Steam, argon, and nitrogen are rather closer together than they are in respect of their accelerating influence, but the ratio of the effects of helium and nitrogen corresponds quantitatively to that of the reciprocals of the D values. Thus it seems almost certain that the whole effect of the inert gases can be accounted for by the chain theory. The true values of D are very hard to arrive at theoretically, since the chain propagators do not diffuse through pure nitrogen or helium or other inert gas, but through a mixture of this with oxygen and hydrogen.

[†] Gibson and Hinshelwood, loc. cit.

Semenov† has calculated the inert gas effect to be expected when certain specific assumptions are made about the nature of the chain carriers (they are assumed to be H and HO_2). If λ is the mean free path of a given chain carrier in a given one of the gases present, then the total number of collisions that the chain carrier makes, from the time of its formation to its end, is $\frac{3\pi x^2}{4}(\sum \lambda^{-1})^2$, where x measures the linear dimensions of the vessel. With some approximations he then calculates that in Gibson and Hinshelwood's experiments 300 mm. nitrogen should accelerate the reaction 4·0 times compared with the 4·61 observed at 559°, while 300 mm. helium should accelerate 1·43 times instead of the 1·75 observed. The result is essentially in agreement with the rougher estimates of Gibson and Hinshelwood, namely that the observed effect of the inert gas is rather greater than that calculated, but is of quite the right order to be expected from the diffusion theory. Semenov attributes the differences to the process of 'secondary activation', which will be referred to later.

The influence of temperature on this reaction is complex. If the logarithm of the rate is plotted against $1/T$, the line obtained has a variable slope owing to the transition from surface reaction to gas reaction. The final slope is high and corresponds to an enormous energy of activation. But this quantity will not have its usual simple significance, since not only the number of chains starting, but also the ease of propagation, the probability of secondary activation, and the rate of breaking vary with the temperature and determine the rate. In the neighbourhood of 830° abs. the increase in rate for 10° is 4·3 when the initial pressure is 400 or 300 mm., in a 250 c.c. vessel. At 200 mm. the ratio is 2·6. With a vessel packed so as to suppress all gas reaction the ratio is 1·39 and independent of the pressure: moreover under these circumstances the ordinary Arrhenius equation is followed.

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† Semenov, *Z. physikal. Chem.*, 1929, B, 2, 169.

Having concluded beyond reasonable doubt that the reaction takes place by a chain mechanism, we are faced with the question of the chemical nature of the chain carriers. From the kinetic relationships alone it is hardly possible to decide definitely between certain alternatives, but some general conclusions may be reached.

In the first place we do not know whether the chain carriers are activated molecules, or whether they are free atoms or radicals of some kind. At first sight, the activated molecule hypothesis seems to be preferable, because it involves fewer specific assumptions, and the part played by activated molecules is familiar in every part of chemical kinetics. On the other hand, the intervention of free atoms and radicals in many photochemical reactions has been definitely proved, and their occurrence in many thermal reactions can now at least be inferred. The fact that inert gases do not retard the reaction is perhaps to be regarded as evidence against the activated molecule theory. The foreign molecules might be expected to deprive the chain carriers of their energy and break the chain. But this argument is not a conclusive one. Energy interchanges between molecules are often highly specific. The light energy absorbed by fluorescein molecules in aqueous solution is not degraded in the innumerable collisions which they suffer with water molecules. Yet increase in the concentration of the fluorescein itself, or the addition of certain specific substances destroys the fluorescence.† Thus it might be possible for activated molecules of hydrogen, oxygen, steam, or hydrogen peroxide to survive collisions with inert gas molecules without loss of activation energy. Nevertheless, that various foreign gases should increase the rate of reaction so nearly in accordance with the predictions of the diffusion theory, and show no sign of exerting any appreciable deactivating influence, seems improbable, unless we suppose the 'activated molecules' to be absolutely exempt from any possibility of deactivation in a simple collision. Free atoms and radicals would of course satisfy this condition in a way that molecules with activation energy could not. The free-radical hypothesis has the further advantage of allowing the photochemical and thermal reactions to be treated in analogous ways. Introducing such an analogy is obviously a simplification, and is to be preferred if possible, but is not necessarily justified. In explaining the breaking of the chains at the wall of the vessel neither hypothesis has any advantage over the other. The breaking probably occurs by a chemical reaction of the chain carriers with gases adsorbed on the wall. Activated molecules or free radicals could equally well take part in such a reaction.

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† Perrin, *Compt. Rend.*, 1927, **184**, 1097.

We may conclude by saying that while there is not conclusive evidence, nevertheless on the basis of analogies and because of the lack of deactivation by inert gases the hypothesis of free atoms and radicals is to be preferred.

It is characteristic of most chain mechanisms that two kinds of active particle appear in alternation, e.g. in the examples already quoted H and HO_2 or H_2O^* and O_2^*. It will be useful first to see what information can be derived without special assumptions, and we will therefore suppose that the following is the sequence of processes. A chain carrier X_O is somehow formed and reacts with H_2 giving some products which include another chain carrier X_H. X_H in turn reacts with O_2 regenerating X_O. This cycle continues indefinitely except in so far as X_O and X_H diffuse to the wall and are destroyed. The assumption is made that each link of the chain involves only binary collisions. The possible occurrence of triple collisions will be considered later. In order to simplify the equations let it also be assumed that X_O is the carrier first formed, and further that X_O is the only one whose destruction at the wall need be taken into account.

Chains will pass through the gas in such a way that a steady concentration of X_O and X_H is attained. These steady concentrations $[X_O]$ and $[X_H]$ only change in so far as the concentrations $[H_2]$ and $[O_2]$ themselves change. Then we have the differential equations:

$$\frac{d[X_O]}{dt} = F_1+k_2[X_H][O_2]-k_1[X_O][H_2]-f_2[X_O] = 0$$

$$\frac{d[X_H]}{dt} = k_1[X_O][H_2]-k_2[X_H][O_2] = 0,$$

whence $$[X_O] = \frac{F_1}{f_2}.$$

F_1 is the rate at which the initial formation of X_O occurs. It is a function of the concentrations. f_2 is the rate at which X_O is destroyed by diffusion to the wall when its concentration is unity; f_2 will be inversely proportional to the concentrations of all the substances present, so that we may put

$$f_2 = \frac{K}{a[H_2]+b[O_2]+c[H_2O]+d[M]},$$

M being any inert gas present. The constants *a*, *b*, *c*, and *d* depend upon the various diffusion coefficients: *a* will be by far the smallest. *K* is a function of the vessel size.

The rate of water formation will be proportional to $[X_O][H_2]$ or to $[X_H][O_2]$ or to their sum. Whichever assumption is made the rate turns out to be proportional to

$$F_1[H_2]\{a[H_2]+b[O_2]+c[H_2O]+d[M]\}.$$

If we assume X_H to be first formed and to be destroyed at the wall, the rate comes out proportional to

$$F_1[O_2]\{a[H_2]+b[O_2]+c[H_2O]+d[M]\}.$$

With both X_H and X_O formed and destroyed the formula is more complicated, and a sort of average of the two given.

Now the first significant fact about the reaction rate is its dependence upon a high power of the hydrogen concentration. In the above formulae the coefficient a must be small compared with b, just as the inert gas effect of helium is small compared with that of argon. Thus the term $a[H_2]$ cannot account for much. The most that the terms other than F_1 can account for, therefore, is a power of the hydrogen concentration rather greater than the first. The rest has to be accounted for by F_1, the function expressing the rate of initiation of chains. Since, under favourable conditions, the rate varies as the cube of the hydrogen concentration, Hinshelwood and Gibson made the hypothesis that the chains were started by the ternary collision process $2H_2+O_2 = 2H_2O$. Their scheme had various unsatisfactory features, including the occurrence of ternary collisions in the course of the chain, and assumptions about specific energy transfers, which, although possible, are not easy to confirm or disprove. The following modification of it:

$$\begin{aligned}
&(1) & 2H_2+O_2 &= H_2O^*+H_2O \\
&(2) & H_2O^*+H_2 &= H_2^*+H_2O \\
&(3) & H_2^*+H_2+O_2 &= H_2O^*+H_2O \\
&(4) & H_2O^* &= H_2O \text{ (at surface)}
\end{aligned}$$

$$\frac{d[H_2O^*]}{dt} = k_1[H_2]^2[O_2]-k_2[H_2O^*][H_2]$$
$$+k_3[H_2^*][H_2][O_2]-k_4[H_2O^*] = 0$$

$$\frac{d[H_2^*]}{dt} = k_2[H_2O^*][H_2]-k_3[H_2^*][H_2][O_2] = 0$$

gives a rate of reaction proportional to

$$[H_2]^3[O_2]/k_4 \text{ i.e. to } [H_2]^3[O_2]\{a[H_2]+b[O_2]+c[H_2O]+d[M]\}.$$

This is in approximate accordance with the facts, a being small in comparison with b. The influence of oxygen on the rate is really rather smaller than the formula predicts, the effect of excess oxygen being in fact not much greater than that of added nitrogen. The variability of the order of reaction can be explained by the simultaneous occurrence of surface and gas reaction, and also by the simultaneous occurrence of more than one energy chain of the above type.

It is not suggested that there is real evidence that energy chains play as important a part in the process as atom and radical chains. But it is as well to realize that the facts are not entirely inconsistent with such a possibility. As we have seen, there are certain general arguments in favour of the material variety of chain in the present example, and we must now consider the matter from this point of view.

Of the various possible material chains the natural one to choose is that most nearly analogous to the photochemical mechanism:

$$(1)\quad H+O_2 = HO_2$$

$$(2)\quad HO_2+H_2 = H_2O_2+H.$$

In this scheme H is the X_H of the previous discussion and HO_2 is the X_O. To bring this scheme therefore into harmony with the facts, the initial rate of formation of H or HO_2 would have to be proportional to a high power of the hydrogen concentration. It is not quite easy to see why this should be so.

In a scheme suggested by Semenov† the great influence of hydrogen concentration is attributed to a process of 'secondary activation'. The hydrogen atom emerging from the reaction $HO_2^*+H_2 = H_2O_2+H$ is likely, according to Semenov, to carry away a large amount of kinetic energy, E_1 calories. If it happens to meet a hydrogen molecule activated thermally to the extent of

$$E = (101{,}000-E_1)$$

calories it can decompose the latter into atoms, thus giving rise to a multiplication in the number of chains. Without going into all the details of Semenov's calculation, we can see the effect of this assumption in the following simple way. The chance that the fast-moving hydrogen atom meets a hydrogen molecule before losing its kinetic energy to something else is

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† *Z. physikal. Chem.*, 1929, B, 2, 169.

$$\frac{[H_2]}{a[H_2]+b[O_2]}$$

in the absence of inert gases or products of reaction. The chance that this hydrogen molecule is activated enough to be dissociated is proportional to $e^{-E/RT}$. Thus the chance of fresh atoms being formed is

$$k[H]\{[H_2]/(a[H_2]+b[O_2])\}e^{-E/RT}.$$

Then we have

$$\frac{d[HO_2]}{dt} = F_1+k_1[H][O_2]-k_2[HO_2][H_2]-f_1[HO_2] = 0$$

$$\frac{d[H]}{dt} = F_1'+k_2[HO_2][H_2]-k_1[H][O_2]+$$
$$+k[H]\{[H_2]/(a[H_2]+b[O_2])\}e^{-E/RT}-f_1'[H] = 0.$$

Neglecting F_1 and f_1 for simplicity, i.e. assuming that all chains start or stop with hydrogen atoms, we have

$$[H] = \frac{F_1'}{f_1'-k\dfrac{[H_2]}{a[H_2]+b[O_2]}e^{-E/RT}}.$$

This factor occurs in the expression for the rate of reaction.

With appropriate values of the constants E and k this expression can vary very rapidly indeed with the hydrogen concentration. When the positive and negative terms in the denominator are not very different a small change in either makes a considerable difference to the rate of reaction. This view of the matter is interesting and has several advantages, besides accounting for the large influence of hydrogen concentration. Semenov shows that it will account for a more than linear dependence of the rate on the inert gas concentration. The latter has the effect of causing a more or less linear decrease in f_1', and, therefore, a more than linear increase in the rate, when f_1' and the negative term are of the same order of magnitude. Also the term $e^{-E/RT}$ increases with temperature rather rapidly, so that the order of the reaction also gets greater, owing to the fact that the two terms in the denominator become more nearly equal.

This process of secondary activation is a combination of a simple atom or radical chain with an energy chain. As regards the primary origin of the chain carriers Semenov suggests that they are formed in suitable impacts of hydrogen molecules on the vessel wall.

The view has frequently been entertained that the chains have their origin at the surface. The evidence for this comes from experiments on the low-pressure explosion, and is not necessarily relevant in the discussion of the high-pressure reaction. In a simple chain without secondary activation, the hypothesis of surface origin, as we have seen, is inconsistent with the relation between speed and vessel diameter. With secondary activation this relation can be reinterpreted. The quantity f_1' in the formula is inversely proportional to the square of the diameter. If the initial centres are formed at the wall, F_1' will vary as area/volume, while if they are formed in the gas F_1' will be independent of the surface area. For formation at the surface the rate will vary as

$$\text{const.}\,\frac{\text{area}}{\text{vol.}}\Big/\left\{\frac{\text{const.}}{(\text{diam.})^2}-\text{const.}\right\},$$

i.e. as

$$\frac{\text{const.}}{d}\Big/\left\{\frac{\text{const.}}{d^2}-\text{const.}\right.$$

while for formation in the gas the rate will be proportional to

$$\text{const.}\Big/\left\{\frac{\text{const.}}{d^2}-\text{const.}\right\},$$

for a given concentration of hydrogen and oxygen. The influence of the negative term is to make the rate more sensitive to variations in the diameter. When the positive and negative terms are of the same order of magnitude we can have a dependence on something approximating roughly to the square of the diameter even when, without the influence of the negative term, the dependence would only be on the first power. Thus, when there is secondary activation, we cannot argue from the experimentally found rate-diameter relation that the initial centres must necessarily be formed in the gas. But in these circumstances the secondary activation would be accounting for the initiation of a large proportion of the chains, so that it would still be true to say that most of them had their origin in the gas phase.

The origin of the first chain centres must be considered also in the light of the work of Pease.† On passing a 2 : 1 hydrogen-oxygen mixture at atmospheric pressure through a pyrex reaction vessel at 520–550° he found that the rate of reaction was very sensitive to the pre-treatment of the surface. The greatest reaction velocity was found after the vessel had been washed with nitric acid and rinsed thoroughly with distilled water before drying, whereas the use of dilute potassium chloride solution as a washing medium slowed down the rate of reaction in a marked manner. The results were not reproducible enough to enable accurate values to be found, but as a rough estimate it could be said that pre-treatment with potassium chloride reduced the velocity to one two-thousandth of its ordinary value. Incidentally the vessels treated with nitric acid and water gave as much as 1 molecule of hydrogen peroxide to each 4 molecules of water in the effluent gases, while no hydrogen peroxide was found in the vessels treated with potassium chloride. If the primary formation of the chains is in the gas phase it is difficult to see how such a great reduction in velocity can be caused by a change in the nature of the walls, for assuming a gas phase origin, the subsequent career of the chains will be unaffected until they strike the wall. If we grant the possibility that the action of potassium chloride is due to a high chain-breaking efficiency, then it must also be assumed that ordinary glass surfaces are relatively poor chain breakers, and that a chain has very many times the chance of being reflected back into the gas phase from such a surface as it has when striking the potassium chloride coated wall. The chain breaking hypothesis is to some extent supported by the work of Taylor and Lavin,[†] who found that potassium chloride was more efficient than glass in catalysing the reaction $H+OH = H_2O$ although it did not increase the velocity of the combination $H+H = H_2$ appreciably. On the other hand, the results can be equally well explained if we assume that increased ease of reaction on the surface results in the release of fewer chain initiators *from* the surface into the gas, and therefore decreases the measured reaction velocity. There would be no need then to assume a high 'reflecting power' for clean glass walls.

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† *J. Amer. Chem. Soc.*, 1930, 52, 5106.

On the whole, it would seem that the evidence favours a wall process as the origin of the chains, although in that case secondary activation in the gas phase must play a fundamentally important part.

It must also be noted that hitherto unpublished experiments have failed to reveal any effect of potassium chloride on the reaction in a silica vessel, under the conditions corresponding to most of the experiments described in the earlier part of this chapter.

In a silver vessel the high-order gas reaction between 540° and 600° is almost completely suppressed.[‡] If a vessel of relatively low surface activity is employed there is a slow reaction, but no evidence of a chain process. The chain reaction is very sensitive to variations in pressure and to the presence of inert gases: in a silver vessel these characteristics disappear and we find almost no dependence of the rate on the pressure of hydrogen and only a first power proportionality to the pressure of oxygen, while inert gases have no accelerating effect. Again there are two possibilities: one is that chains do not get started, because chain initiators do not escape from the wall: the other is that the wall has a high deactivating power for any chains that may have been produced. The former suggestion is in agreement with the known high catalytic activity of silver, which might lead us to expect that any chain-forming atoms or radicals would be held on the surface rather than released into the gas phase. However, it is in conflict with the observation that the introduction of a silica rod into the vessel fails to initiate any observable chain reaction. The essence of the second suggestion is that the 'reflection factor' is much smaller at a silver surface than at a silica surface so that the chains are more efficiently stopped.

[†] *J. Amer. Chem. Soc.*, 1930, **52**, 1910.

[‡] Moelwyn-Hughes, Rolfe, and Hinshelwood, *Proc. Roy. Soc.*, 1933, A, **139**, 521.

The question of an intermediate or of a secondary formation of hydrogen peroxide in the reaction is of some importance. Hydrogen peroxide was isolated in the experiments of Pease referred to above. Thus any chain mechanism which is finally adopted must account for the production of this compound. Later experiments of Pease† were designed to show whether water was formed solely by a secondary decomposition of hydrogen peroxide or whether the two compounds were formed by independent modes of reaction. On varying the rate of flow of the reacting gases through a tube it would be expected that the ratio of water to hydrogen peroxide would be sensibly unaffected if the processes were independent, while if the processes were consecutive, hydrogen peroxide would tend to be the sole product as the rate of flow was increased. The results were, however, inconclusive. The absence of hydrogen peroxide from the products obtained in the vessel coated with potassium chloride remains unexplained at present.

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† *J. Amer. Chem. Soc.*, 1931, **53**, 3188.

VI

THE LOW-PRESSURE EXPLOSION

General.

As has already been explained, if a mixture of hydrogen and oxygen is made at 550° C. and the pressure gradually reduced, the gases explode with a bright flash when a certain pressure is reached.† Immediately above the limiting pressure the rate of reaction may be quite slow, and, moreover, increases as the pressure increases, in the manner considered in the last chapter. If the pressure is below a lower limit, the explosion again fails to occur. Thus we have a new phenomenon appearing between well-defined pressure limits, outside which the reaction velocity may be quite small. In the last chapter it was explained that the rate of combination increased very rapidly with the pressure in the region of higher pressures: at 560° in a 200 c.c. vessel of about 8 cm. diameter the rate would become so great at a total pressure of about 600 mm. that further increase in pressure would cause an explosion. At 150 mm. pressure the rate would have fallen to quite a small value. Yet on further reduction of the pressure an explosion occurs. Evidently, then, the inflammation of the gases occurs by two mechanisms: one, at higher pressures, which may be called the normal mechanism, whereby the reaction takes place so fast that isothermal conditions can no longer be maintained; and the second, at lower pressures, which is of a quite different nature. The variation of the limits of the low-pressure explosion is shown in Fig. 4.

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† (*a*) Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, A, **122**, 610.
(*b*) Hinshelwood and Moelwyn-Hughes, ibid., 1932, A, **138**, 311.
(*c*) Grant and Hinshelwood, ibid., 1933, A, **141**, 29.
(*d*) Kopp, Kovalsky, Sagulin, and Semenov, *Z. physikal. Chem.*, 1930, B, **6**, 307.

These will be referred to throughout this chapter as (*a*), (*b*), (*c*), and (*d*).

The experimental methods for the investigation of the limits between which the low-pressure explosion occurs

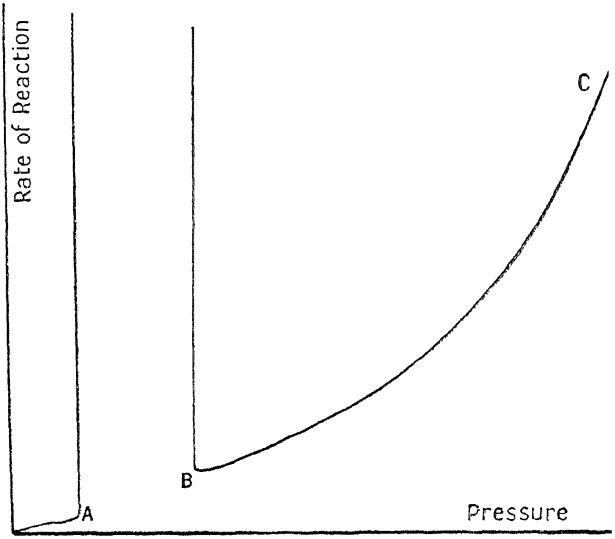

FIG. 4A.

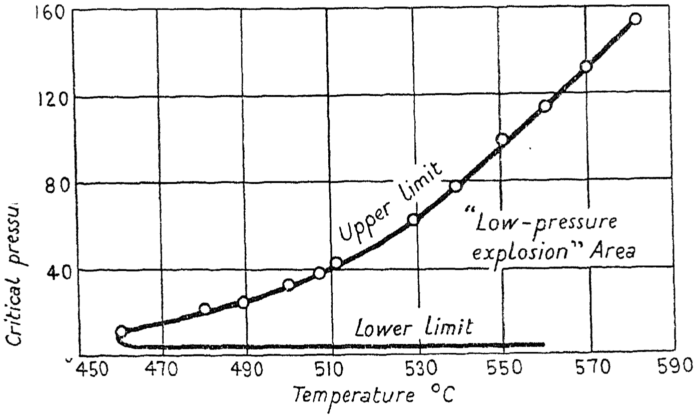

FIG. 4B.

are simple in principle. Oxygen can be added to hydrogen in a reaction vessel without giving rise to an explosion, if the pressure of the hydrogen is above a certain critical value. The same obtains if oxygen is in the vessel and hydrogen is let in, the numerical value of the critical pressure being different in this case. This observation† has been made the basis of practically all the determinations of the upper limit.‡ The gases are successively admitted to the reaction vessel, at relatively high pressures, to obtain a mixture of the desired composition. The mixture is then slowly withdrawn by a pump and the pressure at which explosion occurs is recorded. Such explosions invariably cause the manometer to register a jump, and often are accompanied by an audible sound and a bright flash. The lower limit is more difficult to obtain, because of the relative feebleness of the explosion at this boundary.§ The usual procedure involves premixture of the gases, which are then admitted to the reaction vessel. By a repeated process of trial and error the pressure is found at which admission can occur without the production of a feeble flash.‖ In the case of hydrogen and oxygen this requires rather careful observation using a specially constructed furnace with a suitable window for inspection of the reaction vessel. A flow method can also be employed†† for determining the upper limit. The pre-mixed gases pass through a reducing valve into the reaction vessel, from which they are removed through another valve leading to the pump. The pressure is allowed to reach a steady value and the temperature is gradually increased until explosion occurs.

Semenov and others‡‡ also investigated the lower limit by a manometric method, following the reaction of gases which were initially at a pressure slightly greater than the lower limit. Under these conditions they state that the combustion proceeds until the residual pressure of hydrogen and oxygen has dropped to the lower limit, subsequent reaction being negligible. This phenomenon does not seem quite easy to understand, though the results of the application of the method seem to be in general agreement with those of other observers.

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† Ref. (*a*).
‡ Refs. (*a*) and (*c*).
§ Ref. (*a*).
‖ Ref. (*b*).
†† Ref. (*d*).
‡‡ Ref. (*d*).

All the facts about the low-pressure explosion can be well accounted for by the hypothesis of branching chains.[†] This will now be explained. Alternative hypotheses and the objections to them will be dealt with in a separate section later.

The branching chain hypothesis is as follows. In a chain reaction it may happen that occasionally two or more active centres (activated molecules, radicals, or atoms) are produced instead of one. For example, we might have normally the step $HO_2+H_2 = H_2O_2+H$, where H continues the chain. But if the molecules H_2 and HO_2 had enough energy, the process $HO_2+H_2 = 2OH+H$ might occur, and all three particles might be able to continue the chain. This example simply illustrates what is meant by branching: we are not making at the moment any actual hypothesis about the nature of the molecular species involved. If branching occurs, then the rate of reaction will increase indefinitely, except in so far as the multiplication of the chains is kept in check by deactivation processes. One such deactivation process depends upon the diffusion of the chain carriers to the wall of the vessel, where they are adsorbed or destroyed by reaction. By the balancing of chain branching and the diffusion of the active centres to the wall of the vessel Semenov first explained the sharp passage from very slow reaction to explosion in the oxidation of phosphorus as the pressure increases. At the lowest pressures the diffusion to the walls is easy enough to keep the branching in check: as the pressure increases, the diffusion is impeded. At a certain pressure the rate of increase of chains by branching just exceeds the rate of destruction. The rate of reaction now ceases to be steady, and the chemical change accelerates to explosion. The acceleration takes place in an unobservably short time, since the time scale of the molecular happenings is so small. Thus there is the appearance, as the pressure limit is passed, of the discontinuous transition from very slow reaction to explosion. Shortly afterwards Hinshelwood and Thompson† observed the upper limit in the hydrogen-oxygen explosion, and extended the Semenov theory, supposing that a lower limit appeared when the diffusion to the walls failed to balance the chain branching, and an upper limit when a gas deactivation process, increasing more rapidly with pressure than the chain branching, once more made an equilibrium possible.

[†] The possibility of chain branching is first raised in the paper of Christiansen and Kramers, *Z. physikal. Chem.*, 1923, **104**, 451. The specific application to explosive combustion processes is due to Semenov in connexion with the lower limit in the oxidation of phosphorus, *Z. Physik*, 1927, **46**, 109. The part played by such processes in the hydrogen-oxygen reaction and the extension to the upper limit was discussed by one of the present authors and his collaborators in papers starting with ref. (*a*) above.

From the general theory of chain reactions it can easily be shown that the rate is given by an expression of the following form:

$$\frac{F(c)}{f_s+f_g+A(1-\alpha)}.$$

$F(c)$ depends upon the rate of initial production of chain carriers. f_s measures the rate of destruction by diffusion to the wall, and is thus a function of the pressure and the vessel size. f_g measures the rate of deactivation by collisions in the gas phase, and is thus a function of the concentrations. α is the number of centres produced from one initial one in the branching process, and A, according to circumstances, is a constant or a function of the various concentrations. If there is branching $(1-\alpha)$ is negative. The rate becomes very large and passes into explosion when the negative term nearly balances f_s+f_g. Since f_s decreases and f_g becomes greater as the pressure is increased, we can see how there may be both a lower and upper limit of pressure between which the balancing of the negative term is impossible. As these limits are approached the rate increases indefinitely and very rapidly. Between them there is explosion. In these latter circumstances the above formula ceases to have a physical meaning, since its derivation depends upon equating the rate of branching and the rate of deactivation. The formula shows when the equilibrium just ceases to be possible, but naturally cannot be used for the region where the equilibrium is no longer maintained. Negative rates in the formula thus correspond to the explosion region. In what follows the limit will be treated in a different way depending on the direct application of simple kinetic formulae to the particular case, and there will be no need to use the general formula.

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† Ref. (*a*).

The Lower Limit.

All the facts about the lower limit can be accounted for without the introduction of any special hypothesis about the chemical nature of the chain carriers. We shall simply suppose that two kinds of active particle, X_O and X_H, are formed in alternation, and that X_O reacts with hydrogen, while X_H reacts with oxygen. There is no need to make any hypothesis about the exact origin of the first centres: we are only concerned with the question whether those present increase indefinitely by branching or not.

Let X_O react with hydrogen giving X_H, which in turn reacts with oxygen regenerating X_O, and so on until the chain is broken at the wall of the vessel.†

In the course of the progress of the chain to the wall let there be n_1 collisions between X_O and H_2, n_2 between X_O and O_2, n_3 between X_H and H_2, and n_4 between X_H and O_2, where $n_1+n_2+n_3+n_4 = n$. Since X_H only appears when X_O reacts and vice versa (apart from the very small number of fresh chains starting), $n_1 = n_4$.

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† The calculation which follows is an adaptation of that given for the phosphorus-oxygen lower limit by Semenov (loc. cit.).

Since

$$\frac{n_1}{(n_1+n_2)} = \frac{p_{H_2}}{(p_{H_2}+p_{O_2})} \text{ and } \frac{n_4}{(n_3+n_4)} = \frac{p_{O_2}}{(p_{H_2}+p_{O_2})}$$

approximately,

$$n_1 = n_4 = \frac{p_{O_2}\,p_{H_2}}{(p_{O_2}+p_{H_2})^2}n.$$

From the Einstein-Smoluchowsky relation, if d is the diameter of the tube, the number of collisions made during the course of a chain to the wall is approximately $1{\cdot}5d^2/\lambda^2$, where λ is the mean free path. This number must equal n.

We write $$n = 1{\cdot}5\beta^2d^2/\lambda^2.$$

The 'effective' diameter of the vessel is taken not as d but as βd for the following reason. Some of the chains may be 'reflected' from the walls, since the surface may not destroy the chain carriers with perfect efficiency. Any lack of efficiency in this respect will be equivalent to an increase in the diameter of the vessel. The introduction of β gives us a factor in which the qualitative nature of the surface finds expression.† It will appear later that this factor may be of considerable importance.

Taking as an approximation the mean free paths of the various kinds of molecule to be equal, λ is inversely proportional to the total pressure. Thus it may be written

$$\lambda = \lambda_0/(p_{H_2}+p_{O_2})$$

$$n = 1{\cdot}5\beta^2d^2(p_{H_2}+p_{O_2})^2/\lambda_0^2.$$

Thus $$n_1 = n_4 = \frac{1{\cdot}5\beta^2d^2}{\lambda_0^2}p_{H_2}p_{O_2}.$$

The whole basis of the theory is now that at a given collision of X_O with H_2 or of X_H with O_2 the chain may branch. Let the probability of this occurrence at a given collision be ν. Then the average number of times that a chain branches before it terminates its course at the wall is $\nu \times n_1 = \frac{1 \cdot 5\beta^2 d^2 \nu}{\lambda_0^2} p_{H_2} p_{O_2}$. The condition for explosion is that this expression should exceed unity. More chains then start in unit time than are terminated, and the steady state ceases to be possible. When the expression is less than unity there is less than an even chance that a chain will produce another before ending itself, and there is consequently no acceleration to the point of explosion. The condition for the limit is, therefore,

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† Dalton and Hinshelwood, *Proc. Roy. Soc.*, 1929, A, **125**, 294.

$$p_{H_2} p_{O_2} \beta^2 d^2 = \text{const.}$$

In the presence of an inert gas the collision numbers of the above calculation are different. The necessary modification of the calculation leads to the approximate formula

$$p_{H_2} p_{O_2} \beta^2 d^2 \left(1 + \frac{p_M}{p_{H_2} + p_{O_2}}\right) = \text{const.},$$

as the condition for the limit. M is the inert gas.

In deriving this formula differences in the diffusion coefficients are neglected. When these are taken into account† a more complicated relation is found. A good approximation is found to be given by the formula

$$p_{H_2} p_{O_2} \beta^2 d^2 \left(1 + \frac{D p_M}{p_{H_2} + p_{O_2}}\right) = \text{const.},$$

where D is the reciprocal of the diffusion coefficient of the chain carriers through the inert gas.

Qualitatively and, as nearly as can be expected in view of the approximations introduced into the theory, quantitatively, this equation accounts for the facts discovered experimentally about the lower limit.‡

As the pressure of one gas is increased that of the other decreases. There is however only approximate agreement with the simple hyperbolic relation $p_{H_2} p_{O_2} = \text{const.}$, for a given vessel and temperature in the absence of inert gas. The following numbers illustrate the sort of relation found.

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† Melville and Ludlam, *Proc. Roy. Soc.*, 1931, A, **132**, 108.

‡ Ref. (*b*).

1·8 cm. diameter vessel at 550°. Rate of reaction below limit negligible

At limit		
mm.	mm.	
3·12	0·78	2·43
2·30	1·15	2·64
1·65	1·65	2·72
1·07	2·14	2·29
0·86	3·44	2·96

In another and larger vessel there was a more marked departure from the symmetrical relation, in the sense that the product increased considerably as p_{H_2} decreased.

There are several reasons why the simple symmetrical relation cannot be expected to hold exactly. In the first place, the effect of hydrogen is not the same as that of oxygen in preventing diffusion. Secondly, the factor β which measures the qualitative effectiveness of the surface in breaking chains will vary with the nature of the adsorbed gas films, and these in turn will depend upon the composition of the gas phase. It is obvious, for example, that a highly oxidized chain propagator like HO_2 might be removed much more easily by a surface containing an excess of adsorbed hydrogen. This factor, which also explains differences between different vessels of the same size, is probably the most important. Thirdly, although most of the chains are broken at the wall some may be broken in the gas. At the upper limit, as we shall see, gas-phase deactivation becomes all important. But the upper limit occurs at a pressure about 20 to 100 times greater than the lower limit. Thus the contribution of the gas deactivation at the lower limit must be quite small and cannot, in general, be of great importance.

The most striking characteristic of the whole phenomenon is its dependence on the size of the vessel and on the presence of inert gases. Vessels differ qualitatively from one another in the characteristics of their surfaces, and this fact prevents the relation between $p_{H_2}p_{O_2}$ and d^2 predicted by the formula from being accurately fulfilled. Nevertheless the influence of the vessel diameter is very marked, as the following figures, which refer to an equivalent hydrogen-oxygen mixture at 550°, show.

Diameter cm.	$p_{H_2}p_{O_2}$
5·4	0·13
5·4	(0·41)
4·9	0·183
3·2	1·80
1·8	2·94

Inert gases hinder diffusion and so facilitate explosion. According to the formulae given above $1/(p_{H_2}p_{O_2})$ plotted against $\left(1+\frac{p_{\text{inert gas}}}{p_{H_2}+p_{O_2}}\right)$ should give a straight line. The slope of the line should be approximately proportional to the reciprocal of the diffusion coefficient of the chain propagators through the inert gas. This requirement is also fulfilled, the relative slopes of the curves for helium, argon, and nitrogen being about what would be expected. But some gases such as carbon dioxide exert specific effects: they facilitate the explosion less than they should. This is presumably due to specific deactivating influences counteracting their normal influence on the diffusion. Such specific deactivating influences appear more clearly in the study of the upper limit.

The influence of temperature can also be more conveniently discussed in connexion with the upper limit.

The Upper Limit.†

The upper limit is much more reproducible than the lower. It is independent of the diameter of the vessel, and practically independent of the nature of its surface, being the same in vessels of silica, porcelain, and alumina. Inert gases lower the limit, that is, they make the mixture less explosive, and thus appear to contribute to the deactivation processes, in contrast with their action at the lower limit. Helium has much more effect than argon. Moreover, when there is excess of hydrogen the limit is lower than when there is excess of oxygen. These facts suggest that the molecular velocity of the gas has something to do with its effectiveness in preventing the explosion. A simple theory† based upon this idea gives a quantitatively correct account of the effects observed. As in the theory of the lower limit, it is supposed that there is a finite probability ν that the chain branches at a given collision, either of X_O with H_2 or of X_H with O_2, which we can express generally by saying at a collision of X with Y. The theory is now that the branching is prevented if any third molecule arrives and completes a ternary collision while X and Y are still associated. The nature of this process is considered in greater detail later. At the pressure where explosion just ceases to be possible the rate of branching is balanced by the rate of deactivation in ternary collisions. Thus

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† Refs. (*a*), (*c*), (*d*).

$$\nu k[X][Y]$$
$$= Z_{H_2}[X][Y][H_2]+Z_{O_2}[X][Y][O_2]+Z_M[X][Y][M],$$

where M represents any inert gas present. k is the number of collisions of X and Y at unit concentration of each, and the Z factors are proportional to the collision frequencies of the temporary associate or ‘collision complex’ of X and Y with molecules of hydrogen, oxygen, and the inert gas respectively. As the condition for the limit, therefore, we have

$$Z_{H_2}[H_2]+Z_{O_2}[O_2]+Z_M[M] = \nu k.$$

$[H_2]$ and $[O_2]$ are proportional‡ to P_{H_2} and P_{O_2}.

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† Ref. (*c*).

‡ P will be used for the upper limiting value, p for the lower, in this and following paragraphs.

From this equation it follows that, for a given ratio of hydrogen to oxygen, the sum of their partial pressures should decrease linearly with the amount of the inert gas added. This prediction is accurately fulfilled experimentally. Further, in the absence of inert gas the following relation between the partial pressures of hydrogen and oxygen should hold:

$$P_{H_2} = \text{const.} - bP_{O_2},$$

where b is Z_{O_2}/Z_{H_2}. This linear relation is also accurately fulfilled as the following table shows.

Ratio $H_2 : O_2$	P_e (calc.)	P_e (obs.)
1 : 4	165	165
1 : 2	138	143
2 : 3	127	128
1 : 1	115	116
3 : 2	104	104
2 : 1	98	97
3 : 1	91	91

The calculated values are those given by the equation

$$P_{H_2} = 76 - 0{\cdot}325P_{O_2},$$

P_e being $P_{H_2} + P_{O_2}$.

The values of Z, the ternary collision numbers for unit concentrations, depend upon the molecular speeds and diameters. For a ternary collision between some molecule M and the pair XY it can be proved that Z_M is proportional to $\sigma^2_{XYM}/\mu^{\frac{1}{2}}_{XYM}$, where σ_{XYM} is the sum of the molecular diameters of the complex XY and the colliding molecule M. $\mu_{XYM} = \dfrac{m_{XY}\,m_M}{m_{XY}+m_M}$, m_M, etc., being the respective molecular weights. If the sum of the molecular weights of X and Y is large compared with the molecular weight of hydrogen, the calculation is insensitive to the exact value assumed. On this basis Grant and Hinshelwood were able to calculate that the ratio of Z_{O_2}/Z_{H_2} was practically equal to the value required by the experimental relation between the hydrogen and oxygen pressures at the limit, being 0·39, compared with the value 0·33 found for the constant b in the above formula. The calculated value of Z_{He} is 1·77 times as great as Z_{A}. Actually helium is found to have about 1·6 times the effect of argon in lowering the limit.

In general, then, it may be said that the relative speeds and sizes, but especially the speeds, of the various molecules are the principal factors determining the variation of the upper limit with concentration. Thus the theory of gas-phase deactivation in ternary collisions appears extremely probable. In this connexion it should again be emphasized that the upper limit is practically independent of the vessel. Naturally both gas-phase deactivation and surface deactivation must play their parts at both limits. And this may account for slight variations in the position of the upper limit in different vessels, but since the contribution of the surface deactivation factor has become very small at the upper limit in comparison with gas deactivation, only minor variations arise from this cause.[†]

The Influence of Temperature on the Limits.

As appears in Fig. 4B the upper limit moves rapidly in the direction of higher pressures as the temperature is raised. Thus branching must become much easier. The number of ternary collisions concerned in deactivation will vary only slowly with temperature. In the equation

$$Z_{\mathrm{H_2}}[\mathrm{H_2}]+Z_{\mathrm{O_2}}[\mathrm{O_2}] = \nu k,$$

the variation of Z being small, the temperature coefficient of P_e, the upper explosion limit, will be practically that of ν, the probability of branching. This probability presumably depends upon the energy of the colliding molecules: thus P_e should vary with temperature according to an Arrhenius equation:

[†] It may be mentioned here that direct experiment fails to show any difference in behaviour of gases dried by freezing out with liquid air, and gases dried with phosphorus pentoxide.

$$dP_e/dT = E/RT^2.$$

This is found to be so, $\log P_e$ plotted against $1/T$ giving an exact straight line. The value of the energy of activation is 26,000 calories.† This represents the excess energy H_2 must have in order that branching may occur when it

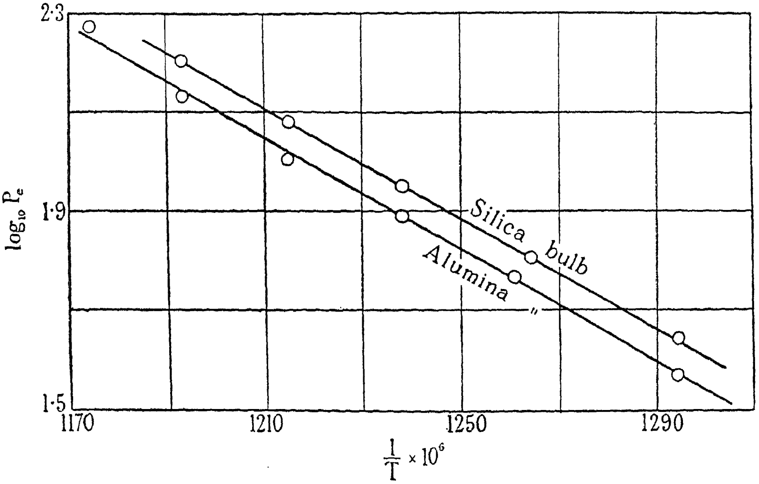

FIG. 5.

is met by X_O, or the energy which O_2 must have when met by X_H. The effect of temperature on the lower limit is a little more difficult to deal with. The condition for explosion at the lower limit is

$$\nu p_{H_2} p_{O_2} \beta^2 d^2/\lambda_0^2 = \text{const.}$$

For a given vessel and composition, neglecting the small variation of λ_0 with temperature,

$$p_{H_2} p_{O_2} = \text{const.}/\nu\beta^2.$$

Therefore $$p_e = p_{H_2}+p_{O_2} = \text{const.}/\nu^{\frac{1}{2}}\beta,$$

whence $$\frac{d\log p_e}{dT} = -\frac{1}{2}\frac{d\log\nu}{dT} - \frac{d\log\beta}{dT}$$

or $$d\log p_e/dT = -\tfrac{1}{2}d\log P_e/dT - d\log\beta/dT.$$

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† Ref. (*a*), (*c*). A determination by Frost and Alyea, *J. Amer. Chem. Soc.*, 1933, **55**, 3227, gives 24, 200.

Thus, if β were constant, $\log p_e$ would decrease with temperature half as fast as $\log P_e$ increases. Thus the effect of temperature on the lower limit will be much smaller than the effect on the upper. The influence of β will depend on the vessel. The reflection factor might normally be expected to decrease as the temperature increased, owing to the increasing certainty that a chain carrier arriving at the wall will be destroyed in a surface reaction. The effect of this is to diminish the absolute magnitude of $d \log p_e/dT$ considerably. Hinshelwood and Moelwyn-Hughes found in one vessel an almost negligible influence of temperature on p_e, except in the lowest temperature region, where it was quite pronounced, while Kopp, Kovalsky, Sagulin, and Semenov with another technique of working found a variation corresponding to a value of $\frac{1}{2}E$ of 14,000 calories, ignoring any changes in β.

The value of E for the upper limit is quite reliable since no surface effects are involved. Thus one collision in $e^{26,000/RT}$ should lead to branching. At 550° C. this factor is of the order 10^7. At one atmosphere pressure at 550° C. the number of collisions made in the passage of a chain to the wall in a 5 cm. vessel is, by the Einstein-Smoluchowsky relation, about $1{\cdot}5 \times 10^{10}$. Thus at atmospheric pressure branching could occur many times, and only gas-phase deactivation prevents explosion. There will be an even chance of branching when the number of collisions made on the way to the wall is 10^7. This will occur at a pressure of $10^7/1{\cdot}5 \times 10^{10}$ atmosphere, or about 0·5 mm. The value found for the lower limit by Moelwyn-Hughes and Hinshelwood in a 5·4 cm. diameter bulb was about 1 mm., and varied rapidly with the size of the bulb. Thus the agreement is good, and shows that no physical impossibilities are involved in the hypothesis of an activation energy for the branching process.†

The next point to consider is whether the number of ternary collisions is likely to be great enough to keep the branching in check at the upper limit. The answer depends entirely upon the time during which X and Y can be regarded as being in collision. If they formed a complex which existed for a finite time and then, as it were, exploded and gave the products responsible for the branching, then, by assuming a long enough life for this complex, we could make it certain that a ternary collision would occur every time. A still simpler mechanism is the following. X meets Y, Y possessing 26,000 calories. They rearrange at once to give AB and C. C is a chain propagator. AB is not itself a chain propagator, but is formed in an activated condition. If it suffers a collision it becomes normal AB, and no branching occurs. But if it escapes collision, it may split up into A and B, either or both of which are chain carriers. This spontaneous decomposition occurs on the average after a time τ. If the pressure is so adjusted that the mean time between collisions is equal to τ, we shall be in the neighbourhood of the upper limit. The separated processes

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† This calculation has not previously been published.

$$X+Y = AB^*+C, \qquad AB^*+M = AB+M^*,$$

with the provision that the second stage shall be completed within a given time, is formally similar to a ternary collision between X, Y, and M, although the actual time intervals involved may be quite different in the two cases. In order to give a concrete illustration of the form of the process, we may consider the following possibility, without in any way committing ourselves to it as probable on other grounds:

$$HO_2+H_2 = H_2O_2^*+H$$

$$H_2O_2^* = 2OH \text{ after average time } \tau,$$

unless previously

$$H_2O_2^*+M = H_2O_2+M^*.$$

The number of times the latter process occurs rather than the former will be proportional to M, and therefore we shall have the same dependence of the limit on the concentrations as in the simple ternary collision hypothesis given earlier.

Below about 450° no explosion occurs at all, the upper and the lower limits coinciding. This means that the probability of chain branching has become so small that any new chains starting have time to end at the wall before branching occurs again, unless the pressure is so high that the upper limit is exceeded. In the ideal case the curves for the upper and lower limits would cut sharply. Actually the lower part may be rounded off as in the experiments of Moelwyn-Hughes and Hinshelwood, but the influence of the factor β will vary from case to case, making the shape of the curve on the lower limit side variable.

Origin of the Chains. Metastability Phenomena.

We have not so far been concerned with the origin of the chains. The condition for explosion depends only upon the branching of such chains as do start, and no matter how few these are, if their number increases progressively, the explosion will ensue. But if absolutely no chains started, the possibility of their branching would not come into the question, even if the conditions for this process were favourable. The state of affairs where none start at all appears sometimes to be realized, and has been called the *metastable* state of the system.[†] In the present example there is prima facie evidence that the first centres must be formed at the wall of the vessel. When crossed streams of hydrogen and oxygen are mixed under conditions of temperature and pressure which would normally lead to the low-pressure explosion, no ignition occurs in the complete absence of a solid wall. The experiment showing this was made by Alyea and Haber[‡] in the following manner. Two narrow porcelain tubes, provided with wiring for electric heating, were mounted at right angles to one another through the walls of an iron box. Hydrogen was passed through one of these tubes and oxygen through the other at rates which could be varied to produce the desired proportions. The tubes were adjusted so that the gas streams crossed about 1 cm. from each nozzle. Nitrogen was admitted to the box in large quantities, and the mixed gases were continuously removed by a pump, so controlled as to give any desired residual pressure when a steady state had been attained. A thermocouple which could be inserted in either stream or at their junction, a quartz window, and a device whereby heated surfaces could be introduced into the crossed stream completed the apparatus. It was thus possible to mix hydrogen and oxygen in the absence of any wall and to control the temperature and pressure. It was found that the crossed streams did not ignite even when the temperatures and pressures were adjusted to values corresponding to points well within the low-pressure explosion area. On bringing a rod of silica, porcelain, or glass into the crossed streams, a flame immediately appeared, but as soon as the surfaces had been removed the flame disappeared. Iron and copper surfaces also gave the explosive flame, but aluminium was without effect.

[†] Hadman, Thompson, and Hinshelwood, *Proc. Roy. Soc.*, 1932, A, 138, 297. [‡] Alyea and Haber, *Z. physikal. Chem.*, 1930, B, 10, 193.

The criticism to which this experiment is open is that, owing to the rapid mixing and continuous dispersal of the gases, chains which might be beginning in the gas phase do not have time to develop to the point of explosion. As we have already said, the time scale of the molecular happenings involved in the evolution from the first branching chains to explosion is very small, but, even so, it is finite, and a time greater than that for which the streams remain in the right condition of temperature and pressure may be necessary. But we shall accept the prima facie evidence that the chains start at the wall, because there is evidence from other sources of the existence of metastable conditions. In these no explosion occurs. As soon, however, as the metastability is removed the explosion occurs, and has exactly the right upper limit.[†] This fact seems to show that only the starting has been inhibited, and not the propagation. The easiest way of explaining a complete failure of the chains to start is by supposing that certain active centres on the wall of the vessel have been subjected to the well-known process of catalytic poisoning.

A pronounced inhibition of the low-pressure explosion of hydrogen and oxygen is caused by the presence of steam.[‡] If care is not taken to ensure that steam produced in the slow reaction does not affect the results, determinations of the limits may be badly vitiated. About 10 mm. of steam will inhibit the explosion entirely. The simplest explanation is that the steam inhibits the wall reaction responsible for the formation of the first centres. In this connexion it may be recalled that steam retards the normal heterogeneous reaction at lower temperatures. It is of course possible that steam exerts a specific deactivating effect in the actual propagation of the chains, but this is less likely in view of the complete absence of any such inhibiting effect on the high-pressure gas reaction. The relation between the upper explosion limit and the steam concentration does not really allow a definite decision between the two possibilities to be made. P_e falls rapidly but continuously as the steam concentration increases, but this can be explained on either basis. We first take the surface poisoning view. If no chains start, there is no limit; if plenty start, the limit is in a constant position however many start; in the intermediate range, where very few indeed start, P_e must run rapidly through intermediate values. On the basis of the alternative view that the steam has a deactivating influence on the propagation, there will naturally be a steady variation of P_e with the partial pressure of steam.

[†] Hadman, Thompson, and Hinshelwood, loc. cit.

[‡] *Proc. Roy. Soc.*, 1931, A, **130**, 646.

Some experiments of Haber and Alyea indicated that pre-treatment of the vessel wall with hydrogen narrowed the limits of the low-pressure explosion. For these experiments very narrow porcelain tubes were used. The results obtained cannot be reproduced with a vessel of normal size even when it is pre-treated with hydrogen for several hours at 550°. The explanation of the difference in behaviour is probably to be found in the varying vessel size. In normal vessels the upper limit varies slightly with the state of the surface, because some deactivation by the walls is superimposed on the principal process which is gas deactivation. In very narrow tubes the wall deactivation will have become relatively much more important, and the chain breaking will be much more sensitive to the nature of the surface.

Alternative Theories.†

Most of the facts about the low-pressure explosion have now been satisfactorily interpreted in terms of the chain theory. Before considering briefly the alternative theories, which all prove inadequate, it will be convenient to summarize the chief phenomena which the chain theory accounts for.

	Lower limit	Upper limit
$H_2 : O_2$ ratio	Approximation to ideal hyperbolic relation between p_{H_2} and p_{O_2}.	Linear relation between partial pressures.
Inert gases	Favour explosion. Argon more effective than helium.	Tend to stop explosion. Argon less effective than helium.
Diameter	Approximation to $1/d^2$ relation.	No influence.
Temperature	Very small effect.	Considerable effect.

The contrasted effects at the two limits are particularly to be noted.

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† Cf. *Trans. Faraday Soc.*, 1932, **28**, 184.

One theory which would explain the existence of an upper and a lower limit is as follows. A surface reaction occurs on certain active points, its rate first increasing and subsequently decreasing as the total pressure of the gas is raised. Such behaviour is not uncommon with heterogeneous reactions, and is easily explained. If the reaction is exothermic, it may liberate heat locally, rapidly enough to inflame the gas as a whole, when the velocity of combination on the active points exceeds some assigned value. There will thus be an upper and a lower limit for the inflammation. If the intense reaction is localized enough on active points, its contribution to the observed change may be very small, except when it has been able to induce ignition. This theory fails entirely to explain the influence of vessel size or the effect of inert gases. It may also be mentioned that the rate of the observable surface reaction does not pass through any maximum as would have to be postulated.

The second type of theory is a purely 'thermal' one, and again attributes the explosion to the non-maintenance of isothermal conditions on active points. The lower limit is reached when the rate of reaction is great enough to heat these points sufficiently, and the upper limit when the cooling effect of the gas is great enough to prevent ignition. This theory also fails to account for vessel-size effects, and, moreover, experiment shows that there is no correlation whatever between the influence of gases on the limit and their thermal conductivities.†

The last theory which need be mentioned explains the upper limit as the boundary between a region where chains can start from the wall and one where they are entirely prevented from starting by an adsorbed gas film of some kind. At a certain pressure this film can be discontinuously stripped off the surface. This fails to explain the lower limit at all, does not explain why the upper limit is independent of the vessel, and influenced by other gases, and is inconsistent with the facts about the surface reaction itself, the investigation of the surface reaction yielding no evidence at all of any such discontinuous changes in the adsorbed films.[†]

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† Ref. (*c*) p. 53.

Conclusion.

It will be seen that all the facts about the limits were explained without any special hypothesis about the chemical nature of the chain propagating species. This is satisfactory in so far as we are interested in the physical aspect of the phenomenon. It also means, however, that little conclusive evidence can be derived from the study of the limits which will enable the atoms, molecules, or radicals concerned to be identified.

The first suggestion[‡] was that hydrogen peroxide played an essential role in the chains. This was made partly to account for the deactivating effect of nitrogen peroxide, which will be dealt with later. But there was no definite evidence. At the time of this suggestion the upper limit was attributed to the destruction of activated hydrogen peroxide formed in the chains by molecules of normal hydrogen peroxide in equilibrium with hydrogen and oxygen. This hypothesis was made simply to illustrate gas-phase deactivation in a concrete way, and had no independent support.

At first[§] it was suggested that the chains upon which the low-pressure explosion depend must be different in kind from those concerned in the high-pressure, steady, gas reaction. The reason for this suggestion was that at the upper limit the explosion is stopped by increase in pressure while the steady chain reaction is facilitated. Later† it became clear that such a contrast is not really necessary. The explosion ceases at the upper limit, because, as we have seen, *branching* of the chains is prevented by ternary collisions. But one particle may, and probably does emerge from the collision which is capable of continuing an unbranched chain. The number of collisions from which the one active particle emerges will of course increase steadily with the pressure.

[†] The possibility was suggested by Alyea, *J. Amer. Chem. Soc.*, 1931, **53**, 1324; it was shown to be inapplicable to the hydrogen-oxygen case by Garstang and Hinshelwood, *Proc. Roy. Soc.*, 1931, A, **134**, 1.

In a still more recent paper Frost and Alyea adopt the branching chain theory. Thus although the 'desorption' theory is possible in principle, there is no need to elaborate its application to the present example (*J. Amer. Chem. Soc.*, 1933, **55**, 3227).

[‡] Ref. (*a*) above.

[§] Ref. (*a*).

We can therefore bring the two sets of facts into harmony if we assume that X_O and X_H alternately react with H_2 and O_2 respectively: that at certain of the collisions, when an extra activation energy of 26,000 calories is available, there occurs a branching of the chain, while, if during this collision, or before the deactivation of a molecule formed in it, collision with any third molecule occurs, the branching is prevented and a normal chain continues. This kind of chain increases in number and length as the pressure increases, and accounts for the high-pressure reaction. The majority of the chains end at the wall, the only function of gas-phase deactivation being to prevent the branching of the chains which leads to the low-pressure explosion.

These are the facts with which chemical hypotheses about the nature of the carriers must be consistent. The further discussion of these hypotheses is reserved for another place.

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† Ref. (*c*).

VII

THE INFLUENCE OF SENSITIZING AND INHIBITING SUBSTANCES

SINCE, as we have seen, reaction chains play so important a part in the combination of hydrogen and oxygen, the addition of foreign substances which interfere with the propagation of the chains may produce the most marked effects. In this chapter the examples discussed will be limited to those which have been studied in connexion with the thermal reaction.

The influence of halogens is a good example of an inhibiting action.† When hydrogen and oxygen are mixed at a total pressure of 450 mm. at 550° C. there is a rapid though non-explosive chain reaction, the characteristics of which have already been described. On the addition of a small amount of chlorine, bromine, or iodine, of the order of 10^{-2} mm., the velocity is reduced to about a quarter of its original value. The inhibiting action is more drastic with bromine and iodine than with chlorine. If the partial pressure of the halogen is increased to about 1 mm., the rate passes through a minimum and then slowly rises, but its value remains much smaller than it would be with a simple hydrogen-oxygen mixture. With iodine the minimum rate is not more than one-tenth of the normal rate.

At relatively low pressures of hydrogen and oxygen there is a sharply defined region in which the mixture explodes spontaneously. Small quantities of halogen rapidly reduce the size of this region, and then wipe out the explosion altogether. Bromine and iodine prevent explosion when their concentration amounts to about one part in ten thousand, but chlorine is much less efficient, a concentration of about one in four hundred being needed.

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† Garstang and Hinshelwood, *Proc. Roy. Soc.*, 1931, A, **130**, 640; *Z. physikal. Chem.*, 1931, Bodenstein-Festband, 656.

The interpretation of these results is not difficult. The extreme reduction in reaction rate at 550° indicates that the chains are broken, by some deactivating effect of the halogen, before they have reached more than a fraction of their normal length. If any one link of a reaction chain is destroyed, all the reaction which would have been contributed by the succeeding links is prevented. Thus a small amount of the chain-breaking substance can exert an influence apparently out of all proportion to its concentration. This is the original Christiansen theory of negative catalysis. The only alternative explanation, in the present example, is that the halogens have a poisoning action on certain centres, on the wall of the vessel, from which chains normally start. But the use of vessels of small diameter, in which the chains are normally much shorter, showed that under these circumstances the inhibiting action of the halogens was much smaller. This result cannot be explained if the inhibition is assumed to take place at the source of the chains on the wall only, and not at any of their links in the gas phase. The passage of the reaction rate through a minimum, and subsequent increase is accounted for by the fact that the heterogeneous reaction taking place on the surface is accelerated at the same time as the gas reaction is inhibited. This can easily be shown by the use of a reaction vessel packed with silica spheres, in which the gas reaction is thoroughly subordinated to the surface reaction. With this system there is no inhibiting effect when halogens are added, but a catalytic reaction increasing with the halogen concentration. Thus the minimum velocity found in an unpacked vessel does not represent the smallest value to which the gas reaction can be reduced, but the residual surface reaction.

The chemistry of the inhibiting action is probably quite simple. In the course of the chain entities such as H atoms, HO_2 molecules, OH radicals, or activated hydrogen peroxide molecules must occur. H atoms can be removed by the reaction $H+I_2 = HI+I$, while the other bodies, containing relatively more oxygen than water does, can be destroyed by reaction with hydrogen iodide, produced thus, $H_2+I_2 \rightleftarrows 2HI$. Analogous processes can occur with the other halogens. One possible reason for the smaller efficiency of chlorine is that the reaction $Cl+H_2 = HCl+H$ can regenerate a hydrogen atom, while the corresponding process is very improbable with the other halogens. The acceleration of the surface reaction is probably a case of intermediate compound catalysis: the reactions $H_2+I_2 \rightleftarrows 2HI$ and $4HI+O_2 = 2H_2O+2I_2$ are known to occur quite readily, the latter being heterogeneous.

Substances may be added to hydrogen-oxygen mixtures which will act as centres from which fresh chains can develop, or which give rise to branching by interaction with normal chain carriers. Among the substances which have been studied are atomic hydrogen, atomic oxygen, and nitrogen peroxide.

Hydrogen atoms, when produced by photochemical methods, possess these sensitizing properties, as has been explained in an earlier chapter. Their behaviour when produced by other methods remains to be considered. Haber and Oppenheimer† led molecular hydrogen through a spark struck between tungsten electrodes, then through a narrow quartz tube to a reaction vessel where the inflowing gases were mixed with a known amount of oxygen. Precautions were taken to prevent the back diffusion of oxygen or active chain carriers into the spark chamber, and, in order to prevent the accumulation of tungsten dust, the connecting passage was frequently cleaned with ammoniacal potassium persulphate. It was found that explosions could be obtained at temperatures as low as 300°, compared with the 450° minimum for non-sensitized hydrogen-oxygen mixtures. A lower critical pressure limit appeared to exist, varying from the value of a few millimetres normally found at 450° to well over 100 mm. at 300°. No upper limit could be found. An attempt was made to find the concentration of hydrogen atoms by passing the mixture from the spark into para-hydrogen and studying the velocity of para-ortho conversion. The results indicated that 2×10^{-4} per cent. of the hydrogen was atomic.

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† Haber and Oppenheimer, *Z. physikal. Chem.*, 1932, B, **16**, 443.

The objections to the above method of working are the uncertainty about the relative concentrations at the point where hydrogen flows into oxygen, and the impossibility of increasing the pressure of molecular hydrogen without increasing the pressure of hydrogen atoms at the same time.

These objections have been avoided in an investigation carried out by Semenov[†] and his collaborators, a static method being used. A discharge tube containing hydrogen at low pressure was heated to the required temperature and a current passed through it until a concentration of hydrogen atoms was established. A mixture of hydrogen and oxygen was then admitted as suddenly as possible, and the pressures necessary to prevent explosion were observed. In this way the concentration of atomic hydrogen could be kept approximately constant while the total pressure was varied, and vice versa. The results showed that a fixed amount of hydrogen atoms simply expanded the explosion limits, and did not cause the upper limit to vanish completely. The reason for its disappearance in Haber's work was probably that the ratio $[H]/[H_2]$ was not variable, and an increase in the amount of molecular hydrogen to a value which would ordinarily carry the system above the upper limit did not now do this, since the limit itself moved steadily farther away, owing to the increasing number of hydrogen atoms. On substituting an aluminium vessel, which ordinarily wipes out the low-pressure explosion, it was found that added hydrogen atoms permitted explosion in a sharply defined region, which expanded with increasing atomic concentration.

[†] *Trans. Faraday Soc.*, 1933, **29**, 606.

An explosion limit, depending upon the control of branching chains, is ordinarily independent of the number of chain centres, and a very great increase in the number of these initiating centres should only make the transition from slow reaction to explosion more gradual, i.e. make the limit less sharp without altering its position. Here, however, we find that the addition of hydrogen atoms alters the limits markedly. We must conclude, therefore, that the shift must have been caused by a modification of the actual chain mechanism. The nature of the mechanism was suggested by Semenov. In an unsensitized hydrogen-oxygen mixture there are relatively few chain initiators, and the probability that the chains will interfere with one another is small. A different situation arises when the number of initiators is increased by the direct addition of hydrogen atoms at high concentration, for the possibility now exists that a chain of the normal sort will be met by one or more of the added atoms, or by the chains which they in turn have started. We can see, in a qualitative manner at least, that such encounters will increase the probability of branching, with the result that the explosion region will be enlarged. The behaviour of the sensitized mixture in the aluminium vessel is due to the fact that the introduction of hydrogen atoms produces the chain centres which would not be spontaneously formed in such a vessel according to Alyea and Haber.†

Oxygen atoms can be produced in an analogous way with an oxygen discharge tube. They influence the reaction very strongly, causing a tremendous enlargement of the explosion region and moving the upper limit completely beyond the zone which was accessible to investigation. Semenov suggested that, in presence of oxygen atoms, chain branching by the following process occurs:

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† *Z. physikal. Chem.*, 1930, B, **10**, 193.

$$O+H_2 = H_2O^*$$
$$H_2O^*+O_2 = H_2O+O+O.$$

The first step gives a molecule of steam containing all the energy of formation. Such a molecule will fly apart into its original components unless the energy is removed in a collision. If the stabilization is effected by an oxygen molecule, the energy will frequently be enough to split the molecule into atoms, since the whole process requires the absorption of 2,000 calories only. Thus two oxygen atoms will appear for the one which started the process. Repetition of this will provide the continued branching which leads to explosion.

Objection to this theory might be made on the basis of the results of Harteck and Kopsch† who found the reactions of oxygen atoms with hydrogen molecules to be inefficient. However, the conditions of their experiments were radically different, the temperature being several hundred degrees lower, and it must be remembered that a reaction requiring a moderate activation energy will become very efficient by the time 500° C. is reached.

The reaction $H_2O^*+H_2 = H_2O+H+H$ is thermochemically even more probable, but this does not lead to the regeneration of the oxygen atom. Thus there is no new kind of branching, and the chains would only develop to the same extent as in the normal unsensitized reaction. The oxygen atoms would give two chains each, but their effect would not go on multiplying.

We now turn to the consideration of nitrogen peroxide. The action of this substance is complex, in that small quantities cause explosion while larger quantities inhibit the explosion once more. In other words, nitrogen peroxide can apparently give rise to chain branching and at the same time act as a chain breaker.

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† Harteck and Kopsch, *Z. Elektrochem.*, 1930, **36**, 714.

H. B. Dixon observed that small amounts of nitrogen peroxide have a remarkable action in lowering the ignition temperature of hydrogen-oxygen mixtures. Gibson and Hinshelwood[†] then found that at temperatures in the neighbourhood of 400° C. there were two critical concentrations of nitrogen peroxide between which explosion of the hydrogen-oxygen mixtures occurred, but outside which the rate of combination was quite small. The matter was further investigated by Thompson and Hinshelwood[‡] and subsequently by Griffiths and Norrish.[§]

The nitrogen peroxide causes explosion at temperatures where hydrogen and oxygen alone are almost completely inert, the upper and lower limits of the normal low-pressure explosion having come together. Thus the explosion must be due to some process quite different from the ordinary branching of the hydrogen-oxygen chain. The action of the nitrogen peroxide must be more profound than merely to increase the number of chains which start. An extra number of chains would only increase the steady reaction velocity without altering the limits, at any rate to more than a secondary extent. The limits are determined by the rate of multiplication of chains which have started, not by the initial number. If we adopt a chain theory of the process at all, we must suppose that the presence of the nitrogen peroxide introduces new possibilities of branching.

The first matter to be decided, therefore, is whether a branching chain theory is to be adopted. Gibson and Hinshelwood pointed out that if the nitrogen peroxide underwent some exothermic reaction the rate of which first increased and then decreased again as the concentration of the peroxide increased, and if ignition of the hydrogen-oxygen mixture occurred when the speed of this reaction exceeded some assigned value, then the upper and lower limits of peroxide concentration could be accounted for. This may be called the thermal theory. The chief difficulty about it is the relative sharpness of the limits. For example, at 400° with 200 mm. hydrogen and 100 mm. oxygen there was explosion with 0·083 mm. nitrogen peroxide, while with 0·076 mm. the rate of reaction was less than 0·2 per cent. per minute. Rates more than one hundred times as great as this can be measured in the high-pressure gas reaction without thermal explosion occurring. Another argument against the purely thermal theory is that increase in the proportion of hydrogen in the mixture makes it more explosive, while it must increase the dissipation of heat on account of its greater thermal conductivity. Finally, one may say that it is probable on general grounds that the physical nature of the explosion phenomenon caused by nitrogen peroxide is not fundamentally different from that occurring with hydrogen and oxygen alone, so that a branching chain hypothesis is a natural one to make. For this reason Thompson and Hinshelwood suggested that nitrogen peroxide could give rise to branching chains, and at the same time could break chains by a kind of 'antiknock' action. The details of their treatment are not given here since a more satisfactory form of the theory, hitherto unpublished, is given later in the present chapter.

[†] *Trans. Faraday Soc.*, 1928, **24**, 559.

[‡] *Proc. Roy. Soc.*, 1929, A, **124**, 219.

[§] Ibid., 1933, A, **139**, 147.

Before proceeding to this it will be convenient to consider the work of Griffiths and Norrish, which led them to a combination of a thermal theory and a branching chain theory. Using one type of reaction vessel, Griffiths and Norrish found explosion limits similar to those found by the previous observers. When the internal space of the vessel was restricted by the introduction of an axial inlet tube they found that there were limits in the same position as before, but that instead of a transition from slow reaction to explosion when the limits were crossed, there was a transition from very slow reaction to very rapid reaction. Under the influence of light of such wave-length that it could dissociate nitrogen peroxide the effect was considerably magnified, but the limits of concentration remained the same as before. The theory suggested on the basis of these observations was that oxygen atoms from the nitrogen peroxide set up chains. These are capable of branching, but the branching is held in check by surface deactivation. Chain carriers can also be removed by the action of nitrogen peroxide. Furthermore, the concentration of oxygen atoms is kept in check by the very efficient process $NO_2+O = NO+O_2$. Thus large concentrations of the peroxide have two deleterious actions on the chain propagation. These assumptions lead to an expression for the rate of reaction which rises to a maximum as the nitrogen peroxide concentration increases, and then falls again. The explosion is supposed to occur when the rate of reaction exceeds some assigned value.

There are two difficulties about this point of view. The first is similar to that raised against the original suggestion of Gibson and Hinshelwood, namely the sharpness of the limits, and especially of the lower limit. According to the Griffiths and Norrish theory the rate of reaction should increase almost linearly with the nitrogen peroxide concentration until it becomes so great that isothermal conditions can no longer prevail. The fact, however, is that just below the lower limit the rate falls abruptly to an almost negligible value. The second objection is that if the limit is reached when the speed attains some assigned value, then the limits should not be the same when the rate of reaction is much increased by illumination. The lower limit should be reached with a much smaller concentration in the illuminated system.

These difficulties disappear if we assume that the explosion depends upon branching chains involving the nitrogen peroxide (or the oxygen atoms derived from it). If the branching is kept in check by deactivating processes, there will be no explosion, while just at the points where the deactivation mechanisms fail to balance the branching there will be a very rapid increase in rate, culminating in explosion.

The question of the non-occurrence of an 'explosion' in the vessel with a central tube must now be considered. In such a vessel, and at the normal limit, an abrupt transition still occurs, but to a very 'rapid reaction'. The rate of this is greater than could be measured in an unpacked vessel without ignition occurring. The simplest view of the matter is that this 'rapid reaction' is itself a type of degenerate explosion. At the limit, the deactivating processes fail to keep the chains in check, and the reaction rate soars up, but the deactivating influence of the walls, by cutting the chains short, prevents the development of a well-marked explosion. The phenomenon of an explosion which does not develop completely has been met in another connexion, namely the combination of carbon monoxide and oxygen.† (In this particular example the degenerate nature of the explosion is probably connected with the action of the reaction products, which hinder the progress of the branching chains, and convert what might have been an almost instantaneous combustion into quite a slow flame.) This type of phenomenon has been variously called a 'slow flame' and a 'degenerate explosion'.‡ It seems highly probable that this is what occurs between the limits observed by Griffiths and Norrish.

Assuming the branching chain theory, nitrogen peroxide must act in two ways: it must cause branching and it must break chains. Moreover, the chain-breaking action must increase according to a higher power of the peroxide concentration than the branching, otherwise there could be no upper limit.

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† Hadman, Thompson, and Hinshelwood, *Proc. Roy. Soc.*, 1932, A, **138**, 297.

‡ Semenov, *Z. physikal. Chem.*, 1931, B, **11**, 464.

It will be convenient to show that most of the facts can be accounted for without, in the first instance, assuming anything about the exact chemical nature of the links in the chain. Chains may be supposed to start from a particle X, formed at a rate F determined by temperature and concentration. X reacts with NO_2 to give Y. At this link branching becomes possible, leading to the regeneration, perhaps after rapid intermediate steps, of α X particles (α being probably 2). We know NO_2 in excess deactivates: moreover, the greater the hydrogen concentration, the higher is the NO_2 concentration required for deactivation. To express this experimental fact, we assume that the branching occurs if Y reacts with hydrogen under appropriate energy conditions, but that if Y meets a second NO_2 it is destroyed. We also assume, for generality, that X can be destroyed at the wall or by some action of the other gases present.

The essential idea, then, is that one collision of X with NO_2 may give branching, but that two successive collisions with NO_2 are deactivating. This could easily be the case if the first collision added an odd oxygen atom to something which thereby became very reactive to hydrogen, while a second collision removed the odd oxygen atom as an oxygen molecule and destroyed the reactive character of the intermediate body.

Thus we have:

X formed initially: rate F

$X+NO_2 = Y+?$, velocity constant k_1

$Y+H_2 = ... = \alpha X+?$, velocity constant k_2

$Y+NO_2 \rightarrow$ chain broken, velocity constant k_3

X destroyed by wall reactions, gas reactions, etc., total rate $f[X]$.

Then

$$\frac{d[X]}{dt} = F-k_1[X][NO_2]+\alpha k_2[Y][H_2]-f[X] = 0$$

$$\frac{d[Y]}{dt} = k_1[X][NO_2]-k_2[Y][H_2]-k_3[Y][NO_2] = 0,$$

whence $$[X] = \frac{F}{f+k_1[NO_2]-\dfrac{\alpha k_1 k_2[H_2][NO_2]}{k_2[H_2]+k_3[NO_2]}}.$$

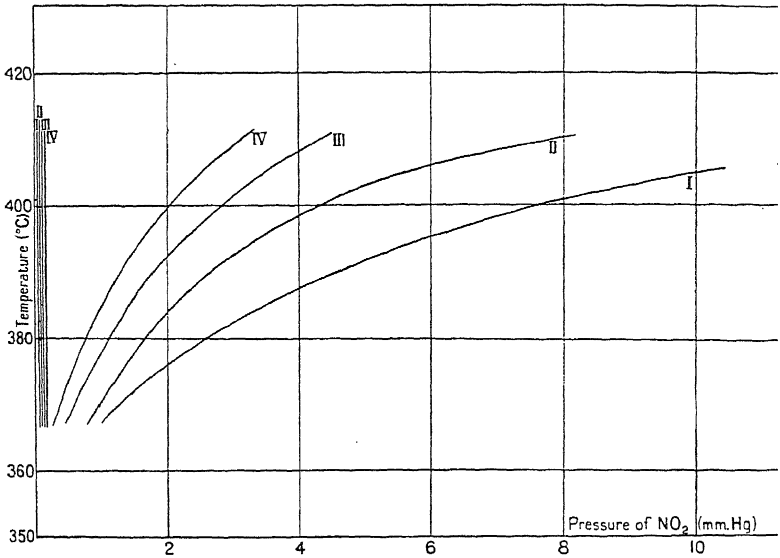
When the negative term in the denominator approaches the positive in value, the value of X, and hence the reaction rate, tends to increase indefinitely. The limits occur when $f+k_1[NO_2]$ ceases to be greater than

$$\frac{\alpha k_1 k_2[H_2][NO_2]}{k_2[H_2]+k_3[NO_2]},$$

i.e. when $f\{k_2[H_2]+k_3[NO_2]\}+k_1 k_3[NO_2]^2$ ceases to be greater than $(\alpha-1)k_1 k_2[H_2][NO_2]$.

When $[NO_2] = 0$, the former term is obviously greater than the latter. As $[NO_2]$ increases, the latter term grows relatively more rapidly at first, and presently the lower limit is reached. At this stage the branching of chains exceeds the deactivation. On further increase of $[NO_2]$ the term $k_1 k_3 [NO_2]^2$, which arises from the deactivation by two successive collisions, becomes great enough to restore equilibrium once more, and the upper limit is then reached. This simple theory accounts, therefore, for the existence of the two limits. It expresses, moreover, the fact that the greater the amount of hydrogen the greater is the amount of NO_2 required to stop explosion. Although increase in the hydrogen concentration favours explosion, it will be seen from Fig. 6 that, for a constant ratio of hydrogen to oxygen, increase in the total pressure causes the limits to move closer together, i.e. makes the explosion occur less readily. Thus oxygen must exert an influence of a deactivating kind. This may be regarded as included in the term *f* of the formula, though it is possible that an extra term expressing some specific action should be added. Nitrogen and the vessel walls also exert deactivating influences. These are included in the term *f*.

The upper limit increases rapidly with rising temperature. This means that the probability of branching



I. 100 mm. H_2 and 50 mm. O_2.
II. 200 mm. H_2 and 100 mm. O_2.
III. 300 mm. H_2 and 150 mm. O_2.
IV. 400 mm. H_2 and 200 mm. O_2.

FIG. 6.

becomes much greater. Thus the branching can only occur when a critical amount of energy is available in the encounter. An apparent value for the heat of activation of the process can be found by applying the Arrhenius equation, and amounts to about 45,000 calories. This, however, expresses the effect of temperature on more than one constant. The large value shows that the chains cannot be simply 'material chains'.

The following diagrams illustrate the difference between the mechanism just described and the one postulated by Griffiths and Norrish. In the theory of the latter authors the relation between rate of reaction and nitrogen peroxide concentration is given by curve *A*. The rate is never indefinitely great since the effect of branching is always held in check by surface deactivation. The acceleration produced by the first portions of nitrogen peroxide is almost linear. In a particular case they predict curve *B*. This is when surface deactivation is insufficient to control branching, and thus the smallest trace of peroxide gives explosion and there is no lower limit. Larger amounts stop branching in the gas phase and thus a single, upper limit is found. The theory we have adopted predicts the relations shown in curve *C*.

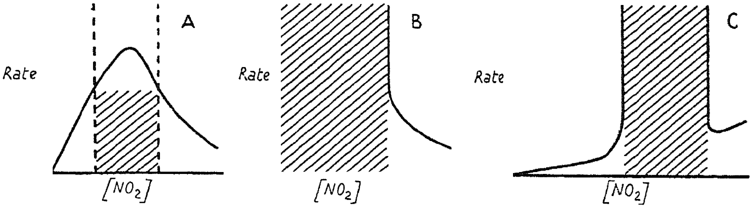


FIG. 7.

Sensitization by Ammonia.†

At 500° a mixture of hydrogen and oxygen reacts very slowly. In presence of 1 or 2 mm. of ammonia there is apparently no immediate effect on mixing, but after a few minutes the pressure begins to change in an autoaccelerating manner and finally there is a sharp explosion. The time required to reach the explosion may vary somewhat, but, for a given set of initial concentrations, the amount of steam formed in this induction period preceding the explosion remains a constant. In the following discussion it will be denoted by $[H_2O]_{in}$.

If the ammonia is left with either the hydrogen or the oxygen alone for a time exceeding that normally required to pass through the induction zone, and then mixed with the other gas, there is no immediate explosion, but, on the contrary, just the same induction period as there would have been normally. Thus the substance which causes explosion must be formed from ammonia and something appearing in reacting mixtures of hydrogen and oxygen but not in either gas by itself.

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† Williamson and Pickles, unpublished experiments.

If the pressure of ammonia is doubled $[H_2O]_{in}$ is reduced to half, and this inverse relationship holds over a wide range. With a constant amount of ammonia, a constant total pressure, and a H_2/O_2 ratio varying from 5·0 to 0·2, $[H_2O]_{in}$ varies directly with the partial pressure of the hydrogen. When all the pressures are increased in a given ratio, $[H_2O]_{in}$ is increased in the same ratio (i.e. there is the same fraction of total reaction as before). The addition of steam in small amounts has little effect on the measurements except slightly to increase the time required to reach explosion.

With quite high concentrations of ammonia a point is ultimately reached at which the explosions cease and are replaced by a fast but measurable reaction.

An increase of temperature by 20° reduces slightly the amount of ammonia corresponding to a given $[H_2O]_{in}$ at explosion. On the other hand, the amount of ammonia required to stop explosion again is almost trebled. When there is an explosion in presence of large quantities of ammonia, some of the ammonia itself appears to be burnt.

In a reaction vessel packed with tubing the phenomena are generally the same, but the sharp explosions are now replaced by rapid, measurable reactions.

We are obviously dealing with the formation of a relatively stable sensitizer from ammonia and some oxidizing agent. Once the oxidation of ammonia has started it is reasonable to suppose that the first product will pass quickly to the most stable form possible at this temperature, namely the equilibrium mixture of nitric oxide and nitrogen peroxide. There is some evidence of this. If an ammonia sensitized mixture is allowed to react almost to the explosion point, and the reaction is then slowed down by the addition of a large quantity of hydrogen, the gases can be withdrawn and tested. They give no reaction with titanium sulphate, indicating the absence of hydrogen peroxide, but a faint test with diphenylamine reagent, indicating the presence of oxides of nitrogen.

Suppose ammonia were oxidized by a chain carrier such as HO_2, the final product being nitrogen peroxide. The steady accumulation of the latter would continue until it approached its lower limit, when inflammation would occur. As explained above, the rate of the nitrogen peroxide sensitized reaction below its lower limit is very small indeed, and we should have to account for the rapid reaction preceding the explosion in the present example. If nitrogen peroxide accumulated at a slow and more or less constant rate, a measurable time would elapse while it passed through a very small zone of concentration immediately bordering the explosion limit. Since the transition, although very rapid, is not mathematically discontinuous, the velocity would increase rapidly as this small zone was traversed. On a concentration scale this region is very small and there would be great difficulty in introducing the exact amount of nitrogen peroxide to obtain a rapid measurable rate, but the slow rate of production of nitrogen peroxide from ammonia provides that, on a time scale, the passage through the zone of rapid reaction is gradual. Most of the steam formed in the induction period is, in fact, generated in the few seconds preceding the explosion, that is, in terms of our hypothesis, during the passage of the nitrogen peroxide concentration through the small zone immediately adjoining the limit. Calculation on this basis shows that the amount of water formed would be expressed by an integral in which $1/[NH_3]$ occurs, the rate of formation of NO_2 being assumed proportional to

$[NH_3]$. This would explain the inverse relation of $[H_2O]_{in}$ and $[NH_3]$, and allow $[H_2O]_{in}$ to be almost independent of the exact value of $[NO_2]$ at the limit, so that a shift of the limit in the presence of steam would not fundamentally alter matters.

The prevention of explosion by large quantities of ammonia indicates that ammonia itself can break chains, its oxidation products being the sensitizers. This chain-breaking property has already been encountered in the photochemical reaction.†

Although formation of nitrogen oxides from ammonia seems to occur, and although the general behaviour of the system corresponds to what would be expected from their gradual accumulation, other facts show that the explanation is more complex. First, the addition of small amounts of nitric oxide to ammonia-hydrogen-oxygen mixtures does not decrease the induction period in the expected manner. Secondly, an influence generally similar to that of ammonia is exerted by cyanogen, which produces no detectable oxides of nitrogen.

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† Taylor and Salley, loc. cit.

VIII

THE CHEMICAL NATURE OF THE CHAIN-PROPAGATING PARTICLES

We have seen that it is often possible to give a fairly complete interpretation of the kinetic phenomena without making very detailed assumptions about the chemical formulae of the various particles which are supposed to be formed in the course of the chain. In some ways this is an advantage, but the ease with which many of the facts can be explained in terms of rather general assumptions involves the less fortunate converse that the kinetic observations seldom provide unambiguous evidence about the nature of the chain carriers. We must, however, endeavour to see how far conclusions about this matter can be drawn.

With regard to the steady gas reaction at higher temperatures, the first hypothesis made was that activated molecules of steam handed on their energy to activate fresh molecules of hydrogen and oxygen. By suitable adjustments this hypothesis could be made to explain many of the facts. The objection to a pure energy chain of this sort is that inert gases appear to have no deactivating effect, as already discussed. For this reason, and also on account of the photochemical analogies and because of the general recognition that free atoms and radicals play a greater part in chemical changes than had hitherto been supposed, 'material chains' were preferred. On the other hand, to explain the low-pressure explosion, the branching of chains must be assumed, and from the influence of temperature on the explosion limits it is clear that the branching only occurs at certain collisions where the requisite energy of activation is available. Thus, as in chemical kinetics in general, the idea of activated molecules cannot be dispensed with. Furthermore, since we have a highly exothermic reaction, and activated molecules of reaction products must often be present, the possibility that collision with them causes the dissociation of hydrogen, or, less probably, oxygen molecules into atoms must be taken into account. This process is termed secondary activation, the special name being convenient although the actual process is simply one form of chain branching.

Among the particles which may be concerned, then, we have activated steam molecules, hydrogen atoms, and oxygen atoms, though the latter will be much less easily formed. In some of the earlier papers on the subject it was suggested that hydrogen peroxide played an important part in the chain process. This compound can indeed be isolated under suitable conditions, and would be the result of the simplest possible bimolecular association reaction of hydrogen and oxygen. One advantage of the assumption was that the mutual destruction of hydrogen peroxide molecules provided a convenient chain-breaking mechanism. The difficulty about assuming hydrogen peroxide as a direct link in the chain, however, is that the only thing it is likely to react with is hydrogen, and this will give activated steam, so that we have to assume an energy chain, which is undesirable for reasons already stated. Thus it may be preferable to regard the formation of the hydrogen peroxide as secondary. From the spectroscopic evidence of the occurrence of OH radicals in hydrogen-oxygen flames, and in the absorption spectrum of steam at 1,200° C., and from the fact that its formation is thermochemically possible, Haber and his collaborators assumed that the hydroxyl radical OH played an all-important part in the combination of hydrogen and oxygen. Photochemically it is known that the reaction can be started by hydrogen atoms, and that the simplest subsequent stage is the attachment of these to oxygen molecules to give HO_2, for the relative stability of which supporting evidence can be found.

If the chains are to be formulated as originating from a free atom or radical, the hydrogen atom is probably the simplest to assume, as it is most easily formed. Haber assumed the next step to be $H+O_2+H_2 = H_2O+OH$. Since, however, a ternary collision can hardly involve the absolutely simultaneous arrival of all the molecules concerned, there is not really a very great difference between this and the alternative whereby the association of the H and the O_2 and the subsequent reaction with H_2 are split into two steps: $H+O_2 = HO_2$, $HO_2+H_2 = H_2O+OH$. There is however a real difference between the formation of H_2O and OH at this step, and the alternative formation of H_2O_2 and H, thus: $HO_2+H_2 = H_2O_2+H$. For the photochemical reaction at low temperatures the latter is certainly to be preferred.

The mechanism of the thermal reaction at higher temperatures may of course be quite different, though it would be satisfactory if the same hypotheses could be made to account for both types. It will be helpful at this stage to consider the low-pressure explosion. The main facts about this, as we have seen, can be accounted for by assuming the formation, in alternation, of bodies X_O and X_H which respectively react with H_2 and O_2. When there is an activation energy of 26,000 calories available at one of these collisions the chain must be capable of branching, but the arrival of a third molecule before the completion of the branching process prevents it altogether. We now observe that we can simplify matters by identifying X_H with the H of the photochemical process, and X_O with the HO_2. The branching can be assumed to occur at the stage HO_2+H_2, which can give 2OH and H if the necessary energy is available. To allow for the fact that the inhibition of this branching by the arrival of a third molecule is by no means an improbable or rare process it is convenient to imagine that the 2OH remain together as an activated molecule of H_2O_2 for a small finite time, on the average, before splitting into two hydroxyl radicals. If, in the interval, the third molecule comes, normal hydrogen peroxide is formed, and then suffers the ordinary rapid decomposition into water and oxygen. The study of the low-pressure explosion does not lend positive support to this adaptation of the photochemical scheme, but is quite consistent with it. Thus the two sets of observations can be grouped under one heading as a working hypothesis.

If HO_2 retains its original energy of formation and reacts with H_2, 38,000 calories are liberated when H_2O_2 is formed, but 10,000 calories are absorbed if the H_2O_2 is split into 2OH. If the HO_2 does not bring its energy of formation into the encounter with hydrogen, then 50,000 calories would need to be provided by the hydrogen for the formation of the 2OH. The actual value of the energy which the HO_2 brings into the encounter will vary, according to whether it has, before meeting hydrogen, met some other molecule, and according to the amount of its energy which this other molecule has removed from it. Thus the extra activation energy needed for chain branching will, on the average, lie between 10,000 and 50,000 calories. The experimentally observed value is 26,000. Thus the branching process postulated seems to be energetically possible. The value 26,000 appears as an average formed in a very complex way, the detailed analysis of which cannot be profitably attempted.

When what is virtually the ternary collision has occurred and prevented branching, then only the H atom is capable of continuing the chain. However, the non-branching chain continues, and the rate of the reaction due to it increases steadily as the pressure increases, and we pass into the region of the 'high-pressure' gas reaction. To account for the great influence of hydrogen concentration on the latter, it is apparently necessary to assume, as already explained, a considerable amount of secondary activation of hydrogen. Other processes, such as the participation of activated steam molecules, may contribute a share to what is quite probably a rather complex series of changes. There is certainly no good evidence to the contrary.

From what has just been said we see that it is possible to interpret in terms of one chemical scheme the photochemical change, the low-pressure explosion, and the thermal gas reaction. The isolation of hydrogen peroxide by rapid cooling of a gas stream can also be accounted for. When the gas reaction finally passes into the explosion characteristic of high temperatures and pressures, still further particles, including ionized atoms, molecules, and radicals may make their appearance.

With regard to the introduction of oxygen atoms and hydrogen atoms we have, according to Semenov,† with the latter, a small, and with the former a very considerable, widening of the explosion region. According to the chain theory the limits should be independent of the number of chains starting, and depend only upon the effective rate of branching. New possibilities of branching must be sought for, therefore, to explain the shift of the limits. When hydrogen atoms are produced by an electric discharge, as in the experiments in question, the concentration reaches a value corresponding to an amount recognizable by ordinary chemical tests (compare R. W. Wood's well-known experiments). Thus the possibility that hydrogen atoms meet particles which are normally chain carriers has to be taken into account. This is what Semenov calls interaction of chains. Normally HO_2 would only react with H_2: if it meets H, as it may do when the atomic concentration is artificially increased, the much more exothermic reaction $HO_2+H=H_2O_2=2OH$, may take place, the probability of branching being very much greater than in the corresponding reaction with the molecular hydrogen. The limits will thus be moved farther apart.

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† Loc. cit.

In the case of oxygen there is no reaction quite so obvious as the above to explain the greater branching probability. Naturally O and H_2 can give H and OH, but this merely means an increase in the number of chains starting. To get widened limits, the O must interact with something which is formed again and again in the chain, in order that one initial branching may be effectively repeated when conditions are favourable. O does not react with HO_2 in any way which suggests itself as obvious. With H we might get an excited OH of short life, which would contain so much energy that it could dissociate the next hydrogen molecule that it met. While we cannot say exactly which process occurs, we at least know that when an oxygen atom interferes with a chain carrier so much energy will be available that a subsequent dissociation reaction leading to branching will be highly probable. Semenov himself, as has already been explained, suggests that activated steam provides energy for the dissociation of oxygen:

$$H_2O^* + O_2 = H_2O + 2O.$$

We now come to the question of the action of nitrogen peroxide, the general theory of which has already been discussed. Norrish and Griffiths found that the thermal interaction of hydrogen and oxygen sensitized by nitrogen peroxide was intensified by light. Since they found that the wave-length threshold where the light began to be active was the same as that for dissociation of the peroxide they concluded that the chains were initiated by oxygen atoms. They confirmed the result of Hinshelwood and Gibson on the existence of an upper and lower nitrogen peroxide concentration, between which limits vigorous interaction occurred. This vigorous interaction, as we have seen, can be regarded as a degenerate explosion. Since the same limits were found for the intensified photochemical interaction as for the less intense thermal change, it was concluded that oxygen atoms play a part in starting the thermal chains also. This conclusion seems to be justified. But even if oxygen atoms start chains, they cannot themselves determine the branching of the chains leading to explosion. If they did this, increase in the light intensity, by magnifying the rate of production of oxygen atoms, would lessen the amount of nitrogen peroxide required to give explosion. Thus the limit would be lowered. But, according to Norrish and Griffiths, the limits are unchanged by illumination. Thus they cannot depend directly upon the oxygen atoms. In the expression for the rate of a branching chain reaction,

$$F(c)$$

increase in the number of oxygen atoms, or other chain starters, increases the numerator. This magnifies the intensity of the interaction at every stage, but cannot change the limits, which depend upon the balancing of the various terms in the denominator. The limits are determined by the branching process. This branching depends upon the interaction with the sensitizer of something in the chain. The concentration of oxygen atoms derived thermally from nitrogen peroxide is very minute indeed, since 71,000 calories are needed for the process $NO_2 = NO+O$, and, moreover, oxygen atoms are very efficiently removed by the process $NO_2+O = NO+O_2$. Therefore the branching itself must depend upon the encounter of one kind of chain carrier with nitrogen peroxide itself. The actual nature of this process is a matter of the general chemistry of the compounds of oxygen, nitrogen, and hydrogen.

In this connexion it would be pure speculation to go much beyond the general consideration of the previous chapter. It appears that some compound is formed capable of breaking up into two parts, each of which can continue a chain. This compound appears, moreover, to be specifically destroyed by nitrogen peroxide, a fact which suggests that it may contain an odd oxygen atom removable as molecular oxygen by the loosely bound oxygen of the peroxide itself. In view of the vast complexity of the chemistry of the compounds of oxygen, hydrogen, and nitrogen there is no difficulty in imagining the intervention of some such body. The instability of the more complex compounds in bulk at high temperatures is, of course, no evidence against their participation in chain reactions. Their existence at ordinary temperatures proves that they are structurally possible. Their thermodynamic instability at higher temperatures means only that they can rearrange to other products on collision. This is precisely the quality necessary in efficient chain propagators.

That quite simple mechanisms involving only such entities as oxygen atoms are inadequate is shown by the behaviour of mixtures of hydrogen and oxygen with small quantities of ammonia. Although at 500° no observable reaction occurs when hydrogen or oxygen alone are left for a short time with ammonia, nevertheless, in the case of the mixture, the ammonia is attacked by some intermediate of the hydrogen-oxygen chain, and converted into an explosion sensitizer, possibly nitrogen peroxide itself. If the transformation of NH_3 into NO_2 is to occur in a series of bimolecular steps, it seems clear that the intermediate stages must involve products other than free atoms: indeed these products would probably contain hydrogen, oxygen, and nitrogen.

We may summarize the whole position by saying that most of the facts about the unsensitized reaction are capable of interpretation by the relatively simple mechanism which, apart from one or two outstanding difficulties, explains the photochemical observations. The action of sensitizing substances shows that other processes must also play a part, and that sometimes these are rather complex.

It must also be said that, although the simplest possible chemical hypothesis is often adequate for explaining the facts about the unsensitized reaction, crucial tests for excluding more complicated possibilities are seldom available. For example, nothing has been said about the possible formation of ozone when oxygen is sparked. This substance may well be introduced along with the oxygen atoms to which the observed effects are usually attributed. The part it plays may be quite an important one. But in a sense ozone is an oxygen atom carried into the system by an oxygen molecule, so that evidently in many respects its behaviour must be similar, and a crucial test for its intervention is difficult to find.

A word should perhaps be said about the influence of water vapour on the reaction. As far as the surface reaction goes, the influence of steam is, usually, definitely to retard the combination. This happens, for example, with gold and silver surfaces, and also with silica and porcelain surfaces. The 'high-pressure' gas reaction is accelerated by steam, but only to an extent comparable with the action of inert gases such as argon, and the diffusion theory gives an entirely satisfactory account of the effect. The 'low-pressure' explosion is inhibited by steam. Thus there is no evidence whatever that steam plays any part in the actual propagation of chains or in the straightforward surface reaction.

Observations are on record to the effect that a very thorough drying of the gases with phosphorus pentoxide prevents them from exploding when heated in a glass tube in a Bunsen burner flame, under conditions where the undried gases would explode. Sometimes a small contraction was found to have occurred when the 'dry' tubes were opened under mercury after the heating. It is also stated that when the gases are very carefully dried and heated by a coil of silver wire, slow combination occurs, but no explosion. The significance of these results is very difficult to estimate. When the slow reaction of the dried gases takes place water is formed, and the system must almost immediately pass through the region of dryness attainable by ordinary experimenters. Why explosion does not set in at this point is hard to see. If it were not for this, one could suppose that complete drying somehow prevented the initiation of any chains. As it is, the more probable explanation seems to be that the drying process introduced impurities, such as phosphorus compounds, which affected either the starting or stopping of chains, or quite possibly, the catalytic activity of the silver wire. In any case the fact remains that in ordinary experience the action of water is more often retarding than accelerating, so that its participation in the actual propagation of the chains cannot be considered a helpful hypothesis to make. (This, of course, does not mean that activated steam may not sometimes act as an energy carrier.)

The chemical nature of the active particle which first starts a chain is difficult to determine, because, from the circumstances of the case most of the chemical change is due to processes which develop from the initial act by independent mechanisms, such, for example, as secondary activation of hydrogen. The first step must evidently be either a dissociation of hydrogen or of oxygen, or else an interaction of the two kinds of molecule. The latter is more probable, because the compensating energy evolution on combination will in general permit an interaction to occur with a lower energy of activation than is required for a dissociation. If both gases are adsorbed at the time of interaction, it seems improbable that any active products will be released as such into the gas phase. Thus the most probable mechanism is an interaction between one impingeing molecule and one adsorbed one, part of the impingeing molecule being held by the adsorbed one and part escaping as an atom or radical. (The conditions under which an activated molecule, such as steam, might escape from a surface with a large relaxation time will not be discussed here, since the advantages, in the present example, of a material chain as a working hypothesis are considerable, as we have already indicated.)

In this connexion we may refer to experiments† in which hydrogen is passed over clean platinum, and the stream leaving the catalyst is tested for the presence of active particles by chemical reagents. Negative results are always obtained, unless the platinum has been previously treated with oxygen, when the presence of active particles can be detected several centimetres from the catalyst.

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† Mitchell and Marshall, *J. Chem. Soc.*, 1923, **123**, 2448; Kobosev and Anochin, *Z. physikal. Chem.*, 1931, B, **13**, 63.

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